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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 6, June 1961

DETECTION OF SELENIUM IN ORGANIC SPOT TEST ANALYSIS

A test is described for the detection of selenium in organic compounds. It is based on the oxidative decomposition with hot concentrated perchloric acid to yield selenic acid, which reacts with hydrazine to give red elemental selenium. Microchemical limits of identification are reached within the technique of spot test analysis.

F. Feigl, *Anal. Chim. Acta*, 24 (1961) 501–504

DETERMINATION OF AMINES AND ALKYL PHOSPHATES IN KEROSENE SOLUTIONS CONTAINING URANIUM AND SULPHURIC ACID

Methods for the determination of amines, alkyl phosphoric acids and tributyl phosphate in kerosene solutions containing uranium and sulphuric acid are described. Amine and alkyl phosphoric acid are determined volumetrically, after removal of interferences, by titration in chloroform solution with a dioxan solution of perchloric acid. Tributyl phosphate is determined by difference between the total phosphorus and the phosphorus from the acid alkyl phosphoric acid.

A. W. Ashbrook, *Anal. Chim. Acta*, 24 (1961) 504–508

SOME POSSIBLE APPLICATIONS OF MASS SPECTROMETRY TO ACCOUNTING PROBLEMS IN CHEMICAL PROCESSING PLANTS

A procedure is described for the determination of the [total Pu]/[total U] concentration ratio for a given solution by an isotopic dilution method. Results obtained for two samples give a mean precision (1σ) of 0.3% for a determination made by a single mass spectrometric analysis. A possible application of the method would be its use for plutonium accounting analyses in a chemical plant processing natural uranium fuel elements, an important feature being the near elimination of the effect of plant sampling errors. An outline is also given of a similar procedure which might be used for the determination of ^{235}U in a plant processing enriched uranium–aluminium alloy reactor fuel.

R. K. Webster, D. F. Dance and L. J. Slee, *Anal. Chim. Acta*, 24 (1961) 509–525

RADIOCHEMICAL SEPARATION OF COBALT

A method is described for the radiochemical separation of cobalt based on the extraordinary stability of cobalt diethyldithiocarbamate. Interferences are few; only very small amounts of zinc and iron accompany cobalt, which is important in neutron-activation analysis.

P. C. van Erkelens, *Anal. Chim. Acta*, 24 (1961) 526–528

SOME REMARKS ABOUT THE USE OF THE BOMB CALORIMETER

In order to reduce the unfavourable influence of unknown thermometer errors, the method for the determination of the calorific value of organic matter in the calorimetric bomb is modified so that in all determinations nearly the same section of the thermometer is used. For the correction of the observed temperature rise a very simple formula is derived from the more elaborate formula of Regnault–Pfaundler.

H. J. Nijkamp, *Anal. Chim. Acta*, 24 (1961) 529–532

DETERMINATION OF FORMIC ACID BY CATALYTIC OXIDATION WITH CERIUM(IV)

A method is proposed for the determination of formic acid by oxidation with cerium(IV) in presence of potassium bromide. The method can also be used for the further oxidation of organic compounds which yield formic acid under ordinary conditions with cerium(IV).

N. K. Mathur, S. P. Rao and D. R. Chowdhary, *Anal. Chim. Acta*, 24 (1961) 533–535

A NEW RAPID SEMIMICRO TITRIMETRIC DETERMINATION OF MERCURY

Mercury(II) (0.5 to 5 mg) can be determined accurately by titration with potassium iodide solution in presence of potassium periodate and carbon tetrachloride as indicator. The simple and rapid method is applicable to many mercurial compounds and preparations; interferences are few.

K. C. Seal, *Anal. Chim. Acta*, 24 (1961) 536–540

HYDRAZINE AS A TITRIMETRIC REAGENT IN IODOMETRY. I

The preparation, standardisation and stability of hydrazine solution is described. The optimum conditions for the titration with hydrazine solution of pure iodine solution of iodine liberated rom oxidants and of excess of iodine left after oxidation of certain reductants have been determined. The advantages of hydrazine over other iodometric reagents are discussed.

K. S. Panwar, N. K. Mathur and S. P. Rao, *Anal. Chim. Acta*, 24 (1961) 541–545

REDOX INDICATORS IN INDIRECT TITRATIONS OF ANIONS

DETERMINATION OF PHOSPHATE IONS BY MEANS OF LEAD NITRATE

An indirect titration of phosphate with lead(II) nitrate solution is proposed; excess of lead is titrated with potassium ferrocyanide in presence of variamine blue as redox indicator.

Z. Gregorowicz, D. Mazońska and D. Prajsnar, *Anal. Chim. Acta*, 24 (1961) 546–547

CHELATES OF 4-HYDROXYBENZOTHIAZOLE WITH THE RARE EARTHS

The rare earth chelates of 4-hydroxybenzothiazole have been prepared and analyzed by a titrimetric method as well as a microgravimetric method. The infrared spectra of these chelates have been determined.

P.-K. Feng and Q. Fernando, *Anal. Chim. Acta*, 24 (1961) 548–554

COLORIMETRIC MICRODETERMINATION OF BORON IN AQUEOUS MEDIA, WITH REAGENTS CONTAINING AZO OR IMINE GROUPS, DERIVATIVES OF THE ACIDS H AND K

(in French)

For the colorimetric microdetermination of boron, 19 dye-stuffs containing imine or azo groups have been examined; only 6 of these were usable and much the best was azomethine-H. This reagent can be used in aqueous media.

R. Capelle, *Anal. Chim. Acta*, 24 (1961) 555–572

FLAME-PHOTOMETRIC DETERMINATION OF LITHIUM IN SILICATE MINERALS (ZINNWALDITCONCENTRATES)

(in German)

The flame-photometric determination of lithium in Zinnwaldit-concentrates was carried out after removal of the interfering elements (Fe, Al, Mn, Ca, K, Na, etc.) either by means of cation and anion-exchange resins or by means of CdO or basic lead carbonate. Flame photometry alone resulted in up to 8% too high lithium values.

J. Liebig and H. Bredehorst, *Anal. Chim. Acta*, 24 (1961) 573–575

THE REACTION OF SCHOENBERG'S REAGENT WITH ELEMENTAL SULFUR

The infrared absorption spectrum of SCHOENBERG's reagent, $(CH_3OC_6H_5)_2C=NCH_2C_6H_5$ has been obtained in the 650–5000 cm^{-1} region. Assignments have been made for all observed bands using group frequency methods.

W. C. NEELY AND H. B. WILLIAMS, *Anal. Chim. Acta*, 24 (1961) 575–578

ON THE USE OF BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AND BIS-ACETALDEHYDE-OXALYLDIHYDRAZONE IN THE ANALYSIS OF COPPER

The reagents bis-cyclohexanone-oxalyldihydrazone (reagent 1) and bis-acetaldehyde-oxalyldihydrazone (reagent 2) and their complexes with copper were examined by spectrophotometry and polarography. The investigations indicated that in solution reagent 1 existed in three tautomeric forms depending of the pH of the solvent. The decomposition of these forms was studied and decomposition schemes are suggested. In the pH range employed for spectrophotometric determination of copper (7–10), solutions of reagent 1 and the copper(II)–reagent 1 complex were found to be very unstable owing to the decomposition of the ligand. Solutions of reagent 2 and its complexes with copper were found to be much more stable. The investigations further indicated that both reagents form copper(II) complexes with ligand–metal ratios 2:1. In addition a colourless copper(I)–reagent 2 complex with two ligands was found polarographically. The existence of a similar complex between copper(I) and reagent 1 is probable.

E. JACOBSEN, F. J. LANGMYHR AND A. R. SELMER-OLSEN, *Anal. Chim. Acta*, 24 (1961) 579-588

DETERMINATION OF STABILITY CONSTANTS

(Short communication)

G. CURTHOYS AND D. A. J. SWINKELS, *Anal. Chim. Acta* 24 (1961) 589

ELIMINATION OF ALUMINIUM INTERFERENCE IN COLORIMETRIC DETERMINATION OF FLUORIDE IN WATER

(Short communication)

M. C. MOREIRA DE ALMEIDA AND C. PULIDO, *Anal. Chim. Acta*, 24 (1961) 590

DETECTION OF SELENIUM IN ORGANIC SPOT TEST ANALYSIS*

FRITZ FEIGL

Laboratorio da Produção Mineral, Ministério da Agricultura, Rio de Janeiro (Brazil)

(Received December 6th, 1960)

Studies of the reactions of organic selenium compounds revealed the need for a reliable test for selenium which if possible should be rapid and suitable for use on a micro scale. No such procedure could be found in the literature and accordingly a study was organized in which organic compounds of selenium were subjected to reductive or oxidative cleavage by the wet or dry method with the hope of arriving at inorganic selenium compounds which are suitable for the methods of inorganic spot test analysis.

In case of a reduction to the gaseous hydrogen selenide, it seemed likely that reaction of this product with sulfurous acid or iodine to yield elemental selenium could be utilized for the purpose at hand. However, it turned out that the desired reduction by warming organic selenium compounds in acid or alkaline milieu with Devarda alloy, zinc, or Raney nickel did not proceed. Although indications of a reaction leading to elemental selenium or hydrogen selenide were observed with Raney nickel, the conditions could not be discovered for a reliable test for selenium. Attempts to produce hydrogen selenide by sintering with sodium formate, through the reaction $2\ NaCOOH \rightarrow (COONa)_2 + 2\ H^\circ$ which yields hydrogen at 250° were completely unsatisfactory. This finding was remarkable in that only reduction to elemental selenium was obtained whereas organic sulfur compounds of all kinds yield hydrogen sulfide when sintered with sodium formate. A rapid spot test for organically bound sulfur is based on this fact[1].

The efforts to arrive at oxygenated selenium compounds through oxidation by the dry or wet methods were more successful. Such products react rapidly with hydrazine in acidic surroundings and on warming to give red elemental selenium:

$$SeO_3^{-2} + NH_2NH_2 + 2\ H^+ \rightarrow Se^\circ + N_2 + 3\ H_2O$$

Sintering with potassium permanganate has been recommended for the quantitative determination of oxyacid-forming nonmetals in organic compounds[2] and this procedure does yield alkali selenite or selenate when applied to selenium-bearing organic compounds. The sintering can be accomplished with tiny amounts in a micro test tube. The cold residue is heated with 1 or 2 drops of concentrated hydrochloric acid until a clear solution results. When the latter is treated with some solid hydrazine sulfate or chloride, red elemental selenium precipitates. The limits of identification are at quantities of materials which correspond to a content of 10–20 μg selenium.

Another kind of oxidative decomposition (in the wet way) is to warm the sample with potassium persulfate and sulfuric acid in the presence of a little silver nitrat as catalyst[3]. The identification limits were satisfactory but certain selenium compounds proved to be very resistant to this treatment and so required several repetition of the wet oxidation by persulfuric acid. Another disadvantage of this oxidation i that it is not likely to accomplish the objective because the catalytic action of th silver ions is incapacitated by the formation of silver halide in the case of organi compounds containing halogens.

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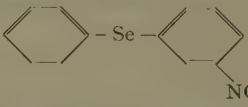
* Translated by RALPH E. OESPER, University of Cincinnati.

Much better and completely reliable results are achieved by means of wet oxidatio with perchloric acid, which was studied in extenso by SMITH[4] and recommended fo the decomposition of organic materials. Perchloric acid, which is not an oxidant i aqueous solution, forms an azeotropic mixture (72.5% $HClO_4$) with water. The mixture boils at 170°. At this temperature, perchloric acid is a remarkably powerful an rapid oxidant and is highly suitable for liberating the metals in organo-metalli compounds. As shown by SMITH, organic-bound sulfur and phosphorus are converte into sulfuric or phosphoric acid. Our studies have shown that warming arsenic- o selenium-bearing organic compounds with perchloric acid rapidly produces arseni or selenic acid. Since perchloric acid does not react with hydrazine in aqueous solution a combination of the oxidative decomposition with perchloric acid and the redo reaction of the resulting selenic acid with hydrazine can lead to a specific test fo organically bound selenium. The heating with perchloric acid is without danger explosive decompositions were never encountered in more than 100 trials. The tes can be accomplished in around 10 min.

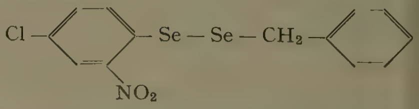
PROCEDURE

A small quantity of the test material or the evaporation residue from 1 drop of it solution in water, alkali hydroxide, alcohol, etc. is placed in a micro test tube an then 1 drop of concentrated (70–72%) perchloric acid is introduced. The mixtur is gradually heated to 205° in a glycerol bath. After about 3 min at this temperature the contents of the test tube are cooled, a drop of a saturated hydrazine sulfat solution is added, and the mixture warmed in a boiling water bath. Depending o the quantity of selenium present, a red precipitate or a pink coloration appears.

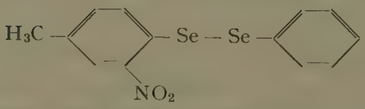
A positive response was obtained with:



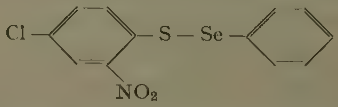
6 μg Phenyl(*m*-nitrophenyl)selenide



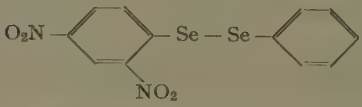
5 μg Benzyl(2-nitro-4-chlorophenyl)diselenid



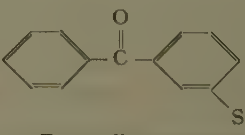
5 μg Phenyl(2-nitro-4-methylphenyl)diselenide



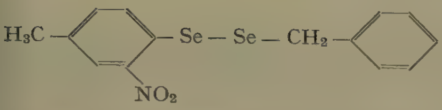
30 μg Phenyl(2-nitro-4-chlorophenylthio)selenid



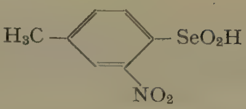
5 μg Phenyl(2,4-dinitrophenyl)diselenide



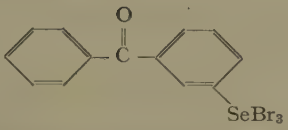
5 μg *o*-Benzoylbenzeneseleninic acid



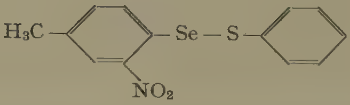
5 μg Benzyl(2-nitro-4-methylphenyl)diselenide



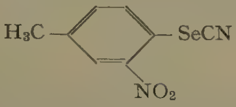
5 μg 2-Nitro-4-methylbenzeneseleninic acid



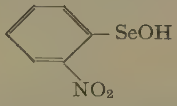
30 μg 3-Benzoylphenylselenium tribromide



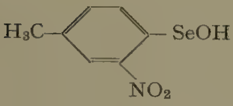
6 μg Phenylthio(2-nitro-4-methylphenyl)selenide



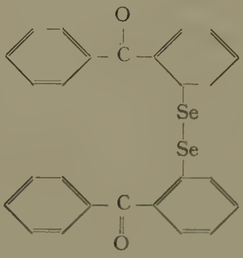
5 μg 2-Nitro-4-methylphenylselenocyanate



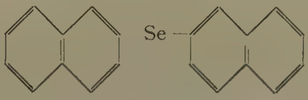
10 μg 2-Nitro-*p*-tolueneselenenic acid



5 μg 2-Nitrobenzeneselenenic acid



30 μg bis-(2-Benzoylphenyl)diselenide



5 μg bis-(2-Naphthyl)selenide

This success in the qualitative detection of selenium in organic materials leads to the expectation that the oxidative decomposition with perchloric acid may likewise be of value in the quantitative determination of selenium in organic materials.

ACKNOWLEDGEMENT

The author is indebted to Mrs. E. KERDMAN-LIBERGOTT for carrying out many of the experiments.

SUMMARY

A test is described for the detection of selenium in organic compounds. It is based on the oxidative decomposition with hot concentrated perchloric acid to yield selenic acid, which reacts with hydrazine to give red elemental selenium. Microchemical limits of identification are reached within the technique of spot test analysis.

RÉSUMÉ

Une réaction à la touche est proposée pour l'identification du sélénium dans des composés organiques. La substance à analyser est attaquée par l'acide perchlorique; l'acide sélénique formé peut alors réagir avec l'hydrazine pour donner du sélénium élémentaire rouge.

ZUSAMMENFASSUNG

Zum Nachweis von Selen (Tüpfelprobe) in organischen Substanzen wird die Substanz mit Pe chlorsäure zerstört und das Selen nach Reduktion mit Hydrazin durch seine rote Farbe nac gewiesen.

REFERENCES

[1] F. Feigl, *Spot Tests in Organic Analysis*, 6th ed., Elsevier, Amsterdam, 1960, p. 95.
[2] F. Feigl and R. Schorr, *Z. anal. Chem.*, 63 (1923) 10.
[3] F. Feigl and A. Schaeffer, *Anal. Chim. Acta*, 4 (1950) 458.
[4] G. F. Smith, *Anal. Chim. Acta*, 8 (1953) 397.

DETERMINATION OF AMINES AND ALKYL PHOSPHATES IN KEROSENE SOLUTIONS CONTAINING URANIUM AND SULPHURIC ACID

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(Received September 20th, 1960)

INTRODUCTION

Mixtures of alkyl phosphoric acids and amines in kerosene solution have been us for the extraction of uranium and vanadium from leach solutions[1]. Experiments ha been carried out in this laboratory on the extraction of uranium from leach solutio by tertiary amine-alkyl phosphoric acid-tributyl phosphate mixtures in kerose solution. Methods for the determination of these constituents were required for complete study of the extraction. A search of the available literature failed to disclo any suitable methods.

EXPERIMENTAL

Determination of amine

Determinations of amine in kerosene solutions containing uranium and sulphu acid have been carried out in this laboratory for several years. Uranium and sulphu acid are removed by shaking the kerosene solution with calcium hydroxide. Sulphu acid is precipitated as calcium sulphate and uranium is adsorbed on the calciu hydroxide. The solids are removed by filtration, and amine is determined on t filtrate by titration, in chloroform solution, with a non-aqueous solution of hydr chloric acid. Thymol blue is used as the indicator.

Application of this method to the determination of amine in the presence of alk phosphoric acids gave high results. The alkyl phosphoric acid caused a turbidity the filtrate which could not readily be removed. This turbidity gave an alkaline rea tion, causing high amine results. The use of calcium acetate in place of the calcium hydroxide overcame this problem, and also removed sulphuric acid as insoluble calcium sulphate. Uranium, however, was not completely removed.

Extraction of uranium can readily be achieved by shaking the kerosene solution with a 20% v/v solution of sulphuric acid before shaking with calcium acetate. After removal of uranium and sulphuric acid, the amine is titrated in chloroform solution, with a dioxan solution of perchloric acid, using thymol blue as the indicator. Tributyl phosphate does not interfere. The reactions occurring are shown in the following equations:

$$(R_3N)_2.H_2SO_4 + (CH_3COO)_2Ca = CaSO_4 + 2\ R_3N.CH_3COOH$$

$$R_3N.CH_3COOH + HClO_4 = R_3N.HClO_4 + CH_3COOH$$

Determination of alkyl phosphoric acid

A mixture of an amine and an alkyl phosphoric acid in chloroform solution behaves as a solution of a dipolar molecule. Consequently, titration of this solution with a strong acid determines the amine, and titration of the same solution with a strong base determines the alkyl phosphoric acid. An excellent indicator for these titrations is thymol blue, having two colour changes, red to yellow at pH 1.7, and yellow to blue at pH 8.9. In the absence of any other acids or bases, this provides a rapid and accurate method for the determination of amine and alkyl phosphoric acid.

Sulphuric acid, if present, must be removed before the alkyl phosphate can be determined. Calcium acetate cannot be used, as it removes some of the alkyl phosphate, giving low results. The problem was overcome by using sodium methoxide, to precipitate the sulphuric acid as sodium sulphate, which is insoluble in chloroform solution.

When a sodium methoxide solution is added to a chloroform solution containing sulphuric acid, amine and an alkyl phosphoric acid, the following reactions occur:

$$(R_3N)_2.H_2SO_4 + 2\ CH_3ONa = 2\ R_3N + Na_2SO_4 + 2\ CH_3OH$$

$$H_2RPO_4 + 2\ CH_3ONa = Na_2RPO_4 + 2\ CH_3OH$$

$$HR_2PO_4 + CH_3ONa = NaR_2PO_4 + CH_3OH$$

$$H_2SO_4 + 2\ CH_3ONa = Na_2SO_4\downarrow + 2\ CH_3OH$$

When thymol blue is used as the indicator, excess of sodium methoxide is indicated by a colour change of yellow to blue. The excess sodium methoxide can then be back-titrated with perchloric acid to a blue to yellow end-point. At this point sulphuric acid has been removed from solution as the neutral sodium sulphate which does not nterfere in the subsequent titrations. Amine is present in solution as the free amine, and the alkyl phosphoric acid as the sodium salt. When titration with perchloric acid s continued to a yellow to red end-point, both amine and alkyl phosphoric acid are titrated according to the equations:

$$R_3N + HClO_4 = R_3N.HClO_4$$

$$Na_2RPO_4 + 2\ HClO_4 = H_2RPO_4 + 2\ NaClO_4$$

$$NaR_2PO_4 + HClO_4 = HR_2PO_4 + NaClO_4$$

The difference between the volume of perchloric acid used to titrate the amine p
alkyl phosphoric acid, and the amine alone, is equivalent to the amount of alkyl ph
phoric acid.

Concentrations of amine and alkyl phosphoric acid are expressed in molarity,
order to simplify the calculations.

Determination of tributyl phosphate

Tributyl phosphate is determined from the difference between the total amount
phosphorus in the solution and that due to the alkyl phosphoric acid. The meth
used for the determination of total phosphorus has been used successfully in t
laboratory for several years.

Determination of amine and phosphoric acids

Reagents

Thymol blue solution, 0.5% w/v in ethyl alcohol. Calcium acetate and chlorofor
analytical-reagent grades. Sodium methoxide solution, approx. 0.1 *N*. Dissolve 2.
of sodium metal in 1 l of methyl alcohol. Perchloric acid solution, 0.1 *N*. Dilute 8.4
of perchloric acid (70%) to 1 l with dioxan. Standardise by any convenient meth

Procedure

Transfer about 30 ml of sample to a 125-ml separating funnel, and add about 20
of 20% v/v sulphuric acid. Shake for 1 min, allow the phases to separate, and disc
the aqueous phase. Repeat this extraction twice. Filter the organic phase throug
double coarse filter paper. Add to a 5-ml aliquot of the filtrate, in chloroform soluti
a few drops of thymol blue solution, and sodium methoxide solution until the solut
colour changes to a deep blue. Add perchloric acid solution to a blue to yellow e
point. Titrate from this point with the perchloric acid solution to a yellow to pur
end-point (Titre *A*).

To the remainder of the uranium-free filtrate add about 5 g of calcium acetate
shake for 1 min. Filter through a coarse filter paper. Titrate a 5-ml aliquot of
filtrate, in chloroform solution, with the perchloric acid solution to a yellow to pur
end-point, using thymol blue indicator (Titre *B*).

$$\text{Amine molarity} = \frac{B \times \text{normality of } HClO_4}{5}$$

$$\text{Alkyl phosphoric acid molarity} = \frac{(A - B) \times \text{normality of } HClO_4}{5}$$

Determination of tributyl phosphate

Place 1 g of magnesium oxide in a small porcelain crucible, and tap to consolid
Pipette 2 ml of the sample onto the magnesium oxide, and place another 1 g
magnesium oxide on top of the sample. Tap to consolidate. Heat the crucible ov
burner until the organic vapours ignite. Remove from the burner and allow to b
until the flame is extinguished. Heat the crucible over a burner until all the carb
has been burned off. Cool and transfer the magnesium oxide to a beaker contain
a few ml of water. Add 5 ml of perchloric acid to the crucible, and 3 ml to the beak

Heat the crucible until strong fumes are evolved, transfer the contents to the beaker and rinse the crucible into the beaker with the water. Heat the beaker to dissolve the magnesium oxide. The phosphorus may be determined by any suitable method. In this laboratory, a molybdovanadophosphoric acid colorimetric method is used.

$$\text{TBP molarity} = \frac{\text{g/l total P} - \text{g/l P from alkyl phosphoric acid}}{31}$$

RESULTS

In these experiments, the amine used was a trifatty amine; the alkyl phosphoric acids used were monoheptadecyl phosphoric and di-2-ethyl-hexyl phosphoric acids. These reagents were only of technical grade, and it was found necessary to determine the apparent molecular weights of each, in order to make up solutions of known molarity. Since very accurate molecular weights were not necessary, they were determined by titrating weighed amounts of the amine and alkyl phosphoric acids with standard solutions of perchloric acid and sodium methoxide respectively. Thymol blue was used as the indicator. Molecular weights are given in Table I. The tributyl phosphate was pure, and the molecular weight used was the theoretical one.

TABLE I

MOLECULAR WEIGHTS OF AMINE AND ALKYL PHOSPHORIC ACIDS

	Calc. mol. wt.	*Apparent mol. wt.*
T.F.A.	—	450
M.H.D.P.A.	336	449
D.E.H.P.A.	322	316

TABLE II

DETERMINATION OF AMINE, ALKYL PHOSPHORIC ACIDS AND TRIBUTYL PHOSPHATE MIXTURES IN KEROSENE SOLUTION*

Amine molarity found	*MHDPA molarity found*	*TBP molarity found*
0.102	0.200	0.106
0.101	0.202	0.107
0.103	0.203	0.109
0.100	0.199	0.109
0.103	0.203	0.104

Molarities added: Amine 0.102, MHDPA 0.202, TBP 0.108

Amine molarity found	*DEHPA molarity found*	*TBP molarity found*
0.196	0.100	0.099
0.198	0.099	0.099
0.199	0.103	0.098
0.196	0.102	0.100
0.200	0.102	0.099

Molarities added: Amine 0.198, DEHPA 0.101, TBP 0.100

* Containing uranium and sulphuric acid.

Kerosene solutions containing known amounts of amine, alkyl phosphoric acid and tributyl phosphate were shaken with a dilute sulphuric acid solution containing uranium. Uranium and sulphuric acid were extracted from the aqueous into the organic phase. After separation of the two phases, the amine, alkyl phosphoric acid and tributyl phosphate were determined by the methods described. Results are given in Table II.

SUMMARY

Methods for the determination of amines, alkyl phosphoric acids and tributyl phosphate in kerosene solutions containing uranium and sulphuric acid are described. Amine and alkyl phosphoric acid are determined volumetrically, after removal of interferences, by titration in chloroform solution with a dioxan solution of perchloric acid. Tributyl phosphate is determined by difference between the total phosphorus and the phosphorus from the acid alkyl phosphoric acid.

RÉSUMÉ

L'auteur décrit une méthode pour le dosage d'amines, d'acides alcoylphosphoriques et de tributylphosphate dans des solutions de kérosène, renfermant de l'uranium et de l'acide sulfurique. L'amine et l'acide alcoylphosphorique sont dosés volumétriquement par l'acide perchlorique, en solution dans le dioxane. Quant au tributylphosphate, il est déterminé par différence entre le phosphore total et le phosphore de l'acide alcoylphosphorique.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Aminen, Alkylphosphorsäuren und Tributylphosphat in Kerosin Lösung, die ausserdem noch Uran und Schwefelsäure enthält. Amine und Alkylphosphorsäuren werden in Chloroformlösung mit einer Dioxan-Perchlorsäurelösung titriert. Die Differenz zwischen der Gesamtmenge Phosphor und der Alkylphosphorsäure ergibt die Menge an Tributylphosphat.

REFERENCE

[1] S. R. Borrowman, P. E. Churchward and J. B. Rosenbaum, *Paper presented at Am. Chem. Soc. Meeting*, San Francisco, April, 1958.

SOME POSSIBLE APPLICATIONS OF MASS SPECTROMETRY TO ACCOUNTING PROBLEMS IN CHEMICAL PROCESSING PLANTS

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INTRODUCTION

The overall accuracy of accounting analyses made for fissile material in a chemical processing plant will usually be limited by difficulties associated with the determination of a valid "plant input figure", for this often involves analyses of the plant feed solution. The isotopic dilution method using solid source mass spectrometry is capable of providing very precise analyses for plutonium[1] or uranium[2,3] in a given solution, but in the application of such a method to the feed solution of a chemical processing plant the overall precision would almost inevitably be controlled by larger errors associated with the determination of sample aliquots, volumes of plant solution, or dilution factors under remote or semi-remote handling conditions. Clearly much would be gained if the isotopic dilution methods could be applied in such a way that either plant sampling errors are eliminated, or at least their significance minimised. The present paper considers this possibility in two typical cases: accounting for plutonium in a plant processing natural uranium fuel elements, and accounting for ^{235}U in enriched uranium–aluminium alloy fuel elements. Where appropriate, published data for the Windscale and Dounreay plants have been used to define typical solution conditions[4,5].

DETERMINATION OF PLUTONIUM IN NATURAL URANIUM FUEL ELEMENTS

Introduction

A previous paper[1] described the determination of plutonium using a ^{242}Pu tracer. Results were obtained for several test solutions and these indicated a precision (1σ) of 0.2% for a single determination. In calculating this figure errors introduced by the dilution of sample and standard were assessed at $\sim$0.1%, so in this case the elimination of these dilution errors could only reduce the overall precision to $\sim$0.18%. However, this latter figure will still include random errors associated with weighing the aliquots of dilute sample and tracer mixed for each determination, and moreover, in this instance the samples were diluted under nearly ideal conditions. In considering the use of this method on a routine basis for the control of a chemical plant it must be recognised that dilution errors could easily be much larger, and in addition uncertainties will be introduced in relating the initial aliquot to the total volume of solution in the plant, and by evaporation of solutions, etc. Once the overall sampling error rises above 0.2% it will be this factor, and not the mass spectrometric analyses, which will control the precision of results obtained for accounting purposes; for example, the overall precision quoted for the isotopic dilution method (including remote pipetting used for uranium in the Idaho Chemical Processing Plant is ~2%, whereas the error involved in mass analyses alone were much smaller[3,6].

In principle sampling errors could be completely eliminated from a plutoniun determination by dissolving a batch of fuel elements containing a known quantit of uranium, and then making a determination of the [Pu]/[U] concentration rati for a small aliquot of the solution. Fuel elements may consist of rods of natural uranium in aluminium or Magnox cans; the rods are "de-canned" by means of a die and hydraulic ram, and are then transferred to the chemical plant[4]. The mass of uraniu rods determined either by weighing after "de-canning", or from the fuel elemen production data, and corrected for the small quantity of uranium consumed by fissio or by conversion to plutonium could give the total uranium input to the plant. Th product of this quantity and the appropriate [Pu]/[U] ratio should then give the tota plutonium input to the plant. In practice a plant may be operated under continuou conditions so plant sampling errors may still be involved in obtaining a representativ aliquot for analysis; however the effect of this should be very much smaller in [Pu]/[U] ratio measurement than is the case when an aliquot is taken for a direc plutonium determination.

The work to be described represents an assessment of the errors involved in determination of the [total Pu]/[total U] concentration ratio by a single mass spectrometric analysis. The samples used were similar to those described previously[1] an contained uranium, plutonium and fission products. Since this work was complete a similar ratio procedure has been described, but using less precise analytical methods namely radiometric analyses for plutonium, and density or X-ray photometric determinations for uranium[7].

Outline of the method

The basis of the present ratio method can be illustrated by examining the equation used to calculate Pu and U concentrations. If an aliquot derived from a plant solutio is mixed with an aliquot of ^{242}Pu tracer, the concentration of total plutonium in th original solution, $[\mathrm{Pu}]_s$, may be found from the following equation:

$$[\mathrm{Pu}]_s = [{}^{242}\mathrm{Pu}]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{M_{239/242} - T_{239/242}}{(\text{mass percentage } {}^{239}\mathrm{Pu})_s} \cdot \frac{239}{242} \cdot D$$

where the subscripts s and t refer to the sample under analysis and the ^{242}Pu tracer $M_{239/242}$ represents the ^{239}Pu/^{242}Pu ratio determined by mass spectrometry for th mixture, and similarly $T_{239/242}$ for the tracer alone; D is the dilution factor for th sample.

Similarly the concentration of total uranium, $[\mathrm{U}]_s$, may be determined by addin an aliquot of ^{233}U tracer and then using eqn. (2), the definitions of terms used bein analogous to those for eqn. (1).

$$[\mathrm{U}]_s = [{}^{233}\mathrm{U}]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{M_{238/233} - T_{238/233}}{(\text{mass percentage } {}^{238}\mathrm{U})_s} \cdot \frac{238}{233} \cdot D$$

Thus if an aliquot of a tracer containing a mixture of ^{242}Pu and ^{233}U is added to sample containing both plutonium and uranium, the $[\mathrm{Pu}]_s/[\mathrm{U}]_s$ ratio is given by eqn. (3), where n is a numerical constant.

$$\frac{[\mathrm{Pu}]_s}{[\mathrm{U}]_s} = n \frac{[^{242}\mathrm{Pu}]_t}{[^{233}\mathrm{U}]_t} \cdot \frac{M_{239/242} - T_{239/242}}{M_{238/233} - T_{238/233}} \cdot \frac{(\text{mass percentage } ^{238}\mathrm{U})_s}{(\text{mass percentage } ^{239}\mathrm{Pu})_s} \tag{3}$$

In this equation the masses (or volumes) of sample and tracer solutions, and the dilution factor are eliminated. The first term of the expression, *i.e.* $n[^{242}\mathrm{Pu}]_t/[^{233}\mathrm{U}]_t$, is obtained by calibration of the mixed tracer against a standard mixture prepared from ^{239}Pu metal and natural uranium; the second term contains either constants for the tracers (Pu, $T_{239/242}$ ~0.005; U, $T_{238/233}$ ~0.0002) or isotopic ratios determined for the mixture of sample and tracer. The third term, consisting of the ratio of the isotopic mass percentages of ^{239}Pu and ^{238}U in the sample under examination, is determined most accurately by taking a second aliquot of sample to which tracer has not been added. However, under certain conditions these quantities may be determined from the mass analysis for the mixture by correction for the quantity of tracer present, and it should then be possible to obtain a value for the following expression by a single mass spectrometric analysis:

$$\frac{M_{239/242} - T_{239/242}}{M_{238/233} - T_{238/233}} \cdot \frac{(\text{mass percentage } ^{238}\mathrm{U})_s}{(\text{mass percentage } ^{239}\mathrm{Pu})_s} \tag{4}$$

Chemical procedure

The chemical procedure used for plutonium has been described in detail elsewhere[1] and only an outline will be given here. A portion of sample is diluted and an aliquot taken containing approximately 0.1 μg Pu (and in this case ~250 μg U). To this is added an aliquot of mixed tracer containing approximately 0.1 μg ^{242}Pu and 250 μg ^{233}U. The dilution factor and the aliquots need not be determined accurately, but approximate values will be required to permit some control over the values of the $^{239}\mathrm{Pu}/^{242}\mathrm{Pu}$ and $^{238}\mathrm{U}/^{233}\mathrm{U}$ ratios produced in the mixture. The mixture of tracer and sample is treated with hydroxylamine hydrochloride followed by nitric acid in order to ensure isotopic exchange, and a solution is then prepared in 8 M nitric acid. About 2% of this solution is taken directly and evaporated to dryness on a microscope slide; this provides ample uranium (~5 μg ^{238}U and ~5 μg ^{233}U) for a mass analysis. The rest of the solution is applied to a column of deacidite FF; uranium and fission products are washed through with 8 M nitric acid, and then plutonium eluted with 0.1 M hydroxylamine hydrochloride, 1 M hydrochloric acid solution. The eluate containing plutonium is evaporated to small volume in a beaker, and then to dryness on a microscope slide. The uranium and plutonium specimens obtained in this way from any one sample are mounted separately on the two side filaments of a triple filament ion source[8] for a mass spectrometric analysis.

A possible source of error in the uranium determinations could be contamination by natural uranium, either airborne or from reagents. This was examined in two stages by blank determinations. The first was made for the initial part of the chemical treatment which involved ~250 μg ^{238}U; the contamination level was 0.002 μg representing an uncertainty of only 0.001%. The second determination was made starting at the point at which a 2% aliquot of solution (~5 μg ^{238}U) was taken and prepared for a mass analysis. This gave an upper limit of only 0.00001 μg, which is again insignificant.

Mass spectrometry

Isotopic analyses were made using an A.E.I. Ltd. M.S.5 mass spectrometer, which is a 12″ radius of curvature 90° sector single focusing instrument incorporating an electron multiplier. The centre filament of the ion source was heated by an unstabilised power supply; stabilised units were used to heat the side filaments. The two side filaments were heated together while they were being "pre-heated" to minimise hydrocarbon background[9], but thereafter were treated separately. The following procedure was usually used for each mass spectrometric analysis. About 40 ^{239}Pu/^{242}Pu ratios were first recorded; then the collector slit width was reduced and about 10 ^{240}Pu/^{242}Pu and ^{241}Pu/^{242}Pu ratios were recorded at a slower scanning speed. A similar procedure was then used to record ^{238}U/^{233}U (~40) and ^{235}U/^{233}U (~10) ratios, but in this case, to reduce the scanning time, a small resistance was switched into and out of the magnet current circuit in order to change the focused ion from ^{233}U to ^{238}U or *vice versa*. The plutonium spectra obtained for samples were generally less precise than those recorded for the earlier work[1], the mean coefficient of variation for scans being 1.13% compared with the previous value of 0.74%. This appeared to be due to a loss in sensitivity arising from a small H.T. leakage between the ion source block and the focus plates.

Results and discussion

Determination of the isotopic mass percentage of ^{239}Pu

Eqn. (3) involves the terms "mass percentage of ^{239}Pu" and "mass percentage of ^{238}U". These could be determined by a mass analysis for an aliquot of sample taken directly without addition of tracer, but in the interests of minimising the number of mass analyses it is worth examining the additional error that would be introduced by making these determinations in the presence of the tracer.

The ^{242}Pu tracer had the following isotopic composition: ^{238}Pu 0.3%, ^{239}Pu 0.4%, ^{240}Pu 0.5%, ^{241}Pu 0.2%, ^{242}Pu 98.4%, ^{244}Pu 0.2%. Thus in addition to determinations of ^{239}Pu, the main isotope in the samples, it should be possible to determine small quantities of ^{240}Pu and ^{241}Pu for samples which may be assumed to contain no ^{242}Pu. This assumption was justified in the present case for the two samples used contained $\ngtr$0.01% ^{242}Pu. If isotopic ratios for sample, tracer, and mixture of sample and tracer are denoted by S, T, and M respectively, then $S_{240/239}$ and $S_{241/239}$ may be found using the following expressions:

$$S_{240/239} = \frac{M_{240/242} - T_{240/242}}{M_{239/242} - T_{239/242}} \quad (5)$$

$$S_{241/239} = \frac{M_{241/242} - T_{241/242}}{M_{239/242} - T_{239/242}} \quad (6)$$

These ratios may then be used to calculate the isotopic mass percentage of ^{239}Pu. Values found in this way for two samples are listed in Table I.

TABLE I

MASS PERCENTAGES OF ^{239}Pu DETERMINED IN PRESENCE OF ^{242}Pu TRACER

	Isotopic mass percentage of ^{239}Pu	
	sample A	*sample B*
Determinations	96.04	95.89
	95.71	96.02
	95.94	95.96
	95.98	95.93
	95.94	95.86
	96.02	95.93
Mean value and standard deviation	95.94 ± 0.12	95.93 ± 0.06
Comparison value	$95.95_2 \pm 0.01_0$	$95.97_7 \pm 0.01_3$

The comparison values were determined using aliquots of "unspiked" sample and these show that the results obtained from mixture analyses contain no serious systematic error.

The precision of a mass percentage determination made in the presence of the tracer is 5–10 times worse than that of a direct determination, but this should still be adequate for the present purposes. Thus in the work described previously[1] the mean precision found for an isotopic dilution determination of the concentration of ^{239}Pu was 0.20%. If a separate mass spectrometric analysis is made to find the isotopic composition of the plutonium sample, then the mass percentage of ^{239}Pu is determined to ~0.01%, so the precision of a determination of total plutonium is also 0.20%. If, instead of making separate determinations of the concentration of ^{239}Pu and of the isotopic composition of the plutonium sample, the whole of this information is obtained from a single mass analysis then, accepting the data in Table I as typical, the precision of a determination of total plutonium will become 0.22%*. Thus in considering the isotopic dilution method for routine determinations of plutonium, it seems that little would be lost by basing determinations on a single mass analysis, for the overall error is increased only from 0.20% to 0.22%, whereas there would be a considerable saving in the mass spectrometric effort required.

The above account omits consideration of the isotope ^{238}Pu. The determination of small quantities of this isotope in samples of the type considered here is subject to interference by ^{238}U. This criticism applies to a result obtained from an "unspiked isotopic analysis" as well as to a mixture analysis so it is probably simpler to make the determination by α-spectrometry.

It may be concluded that a determination of the concentration of total plutonium could be made by a single mass spectrometric analysis with little loss in precision for samples of the present type where the ^{242}Pu content is negligible. However, in considering the application of the method to solutions of dissolved fuel elements it would be necessary to consider the growth of ^{242}Pu with increasing irradiation time. Using published data for the variation of plutonium isotopic composition with irradiation in graphite[10,11] and in heavy water[12,13] moderated reactors it may be shown that the ^{242}Pu correction will be very small for irradiations of ~1000 MWD/tonne, and that if necessary the method could be extended to 5–6000 MWD/tonne by calculating corrections. This point is considered in Appendix 2.

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* This value (0.22%) is obtained by compounding the errors 0.20% for the determination of the concentration of ^{239}Pu and ~0.1% for the determination of the isotopic mass percentage of ^{239}Pu. However, when these determinations are based on the same mass analysis the two errors are not completely independent, and the overall error will be slightly smaller (0.21_2%). This point is discussed in Appendix 1.

Determination of the isotopic mass percentage of ^{238}U

In a similar way the isotopic composition of the uranium in the sample could be obtained from a mixture analysis by correction for the presence of the various tracer isotopes. The isotopic composition of the tracer was as follows: ^{233}U 99.8%, ^{234}U 0.17%, ^{235}U 0.004%, ^{238}U 0.02%. Assuming natural uranium is used as the charge material for the fuel elements, the initial isotopic composition of the sample would be ^{234}U 0.005%, ^{235}U 0.72%, ^{238}U 99.27%. In the course of irradiation the abundance of ^{235}U would decrease and a small quantity of ^{236}U would be produced; these isotopes could be measured in the presence of the tracer. It would be difficult to determine the abundance of ^{234}U, but as it is only present to the extent of 0.005%, changes in its concentration are not likely to be significant. Table II records values found for the isotopic mass percentage of ^{238}U in two samples, and again, in each case, one comparison value obtained using an aliquot of "unspiked sample". As the abundances of ^{234}U and ^{236}U were very small, these isotopes were not determined, so the values listed in the Table are based only on the measurement of either ^{235}U/^{233}U and ^{238}U/^{233}U ratios, or ^{235}U/^{238}U ratios.

TABLE II

MASS PERCENTAGES OF ^{238}U DETERMINED IN PRESENCE OF ^{233}U TRACER

	Isotopic mass percentage of ^{238}U	
	sample A	*sample B*
Determinations	99.32 99.28 99.32 99.34 99.32 99.31	99.28 99.31 99.32 99.32 99.31 99.32
Mean value and standard deviation	99.32 ± 0.02	99.31 ± 0.02
Comparison value	$99.32_4 \pm 0.00_2$	$99.32_6 \pm 0.00_2$

Again the precision of a single determination is ~10 times worse than that achieved by a careful analysis of an "unspiked sample", but even so the random error of 0.02% is insignificant for the present purposes.

Calibration of the mixed ^{242}Pu–^{233}U tracer

Eqn. (3) also includes the term $[^{242}\text{Pu}]_t/[^{233}\text{U})_t$. This concentration ratio for the tracer is determined by an isotopic dilution calibration in which aliquots of tracer are mixed with aliquots of a mixed uranium–plutonium standard. Apart from the mass spectrometric determinations the only sources of random error are those involved in preparing the uranium–plutonium standard. Once weighed quantities of plutonium and uranium have been mixed, subsequent dilutions do not alter the [Pu]/[U] ratio, so in principle errors associated with the use of standard flasks and pipettes are eliminated. In practice, in view of the large concentration ratio, a plutonium metal standard is weighed, dissolved, and a suitable aliquot added to a flask containing a weighed quantity of U_3O_8, but the overall error for this stage can be made quite small. The mixed standard is then diluted to give a plutonium concentration of $\sim$0.1 μg/g, and aliquots mixed with aliquots of the tracer. The results of the calibration are recorded in Table III.

TABLE III

CALIBRATION OF ^{242}Pu/^{233}U TRACER

$\frac{[^{242}Pu]_t}{[^{233}U]_t}$	*Mean value and standard deviation*
0.0003080	
0.0003087	
0.0003087	0.0003088 ± 0.0000005
0.0003090	
0.0003093	(C.O.V. 0.17%)
0.0003094	

The precision (1 standard error) for the mean value of the mass spectrometric determination of the $[^{242}Pu]_t/[^{233}U]_t$ ratio is thus 0.07%. If this is combined with errors arising from the determinations of the isotopic mass percentages of ^{239}Pu and ^{238}U (made in this case for a separate aliquot of standard) and dilution errors, the overall calibration error becomes 0.08%. It should be noted that this value does not include errors arising from uncertainties in such factors as stoichiometry of U_3O_8, etc.

Determination of the [Pu]/[U] ratio for samples

The mixed tracer was used to determine the [total Pu]$_s$/[total U]$_s$ concentration ratio for two samples. For each determination measurements were made of the $M_{239/242}$, $M_{240/242}$, $M_{241/242}$, $M_{238/233}$, and $M_{235/233}$ mixture ratios in a single mass analysis and used with the following equation:

$$\frac{[Pu]_s}{[U]_s} = \frac{[^{242}Pu]_t}{[^{233}U]_t} \cdot \frac{233}{242} \cdot \frac{239(M_{239/242} - T_{239/242}) + 240(M_{240/242} - T_{240/242}) + 241(M_{241/242} - T_{241/242})}{238(M_{238/233} - T_{238/233}) + 235(M_{235/233} - T_{235/233})} \qquad (7)$$

Results obtained in this way are recorded in Table IV.

The values found for the precision of a single determination of the [Pu]/[U] ratio re 0.31% and 0.22% for the two sets of results respectively, giving a mean value of .27%; allowing for uncertainties in the calibration of the tracer gives an overall ean precision of 0.28%. The last column of Table IV records the coefficient of ariation calculated for each result from the observed random errors in the various sotopic ratios measured for the mixture. It is clear that these precision measures re consistent with the observed variation of the results for the [Pu]/[U] ratio, and hat if the method were to be used on a routine basis in a chemical plant, they could provide a means of control over analyses. This point has been discussed in detai elsewhere for plutonium determinations[1].

Thus the isotopic dilution method may be used to determine the [Pu]/[U] concentration ratio for a solution containing both of these elements; the precision (1σ is ~0.3% for a result based on a single mass spectrometric analysis.

TABLE IV

RESULTS FOR [Pu]/[U] RATIO DETERMINATIONS

Sample	*[total Pu]/[total U]*	*Mean value and standard deviation*	*Precision calculated from mass analysis* %
	0.0004120		0.14
	0.0004120		0.17
A	0.0004122		0.12
	0.0004126		0.19
	0.0004127		0.35
	0.0004154		0.41
		0.0004128 ± 0.0000013 (C.O.V. 0.31%)	
	0.0004072		0.19
	0.0004075		0.19
B	0.0004076		0.25
	0.0004083		0.14
	0.0004086		0.14
	0.0004096		0.17
		0.0004081 ± 0.0000009 (C.O.V. 0.22%)	

Corrections required in the calculation of the quantity of uranium present in a given ma of fuel elements

The total quantity of plutonium present in a solution of dissolved fuel elemen will be given by the product of the measured [Pu]/[U] ratio and the total quantit of uranium present, so in addition to the random error of 0.3% noted above the fin result for the quantity of plutonium will also involve uncertainties in relating t quantity of uranium to the mass of fuel elements; thus corrections will be require for loss of uranium both by fission and by conversion to plutonium. In the interes of making a complete investigation the preceding account has been based on t determination of the concentration of total uranium, and corrections for the quantit of ^{235}U transmuted and ^{236}U produced could be calculated from the uranium ma spectrum. However, it would in fact be simpler to omit consideration of these isotop (and ^{234}U) in the calculation of both the concentration ratio and the mass of uraniu for then the only correction required will be for loss of ^{238}U during the irradiatio Deletion of the term ($M_{235/233} - T_{235/233}$) from eqn. (7) will give a determination the [Pu]/[^{238}U] concentration ratio. The quantity of ^{238}U present in a batch irradiated fuel elements will be given by the product of the mass of fuel elements a the original isotopic mass percentage of ^{238}U provided a correction is made for t loss of ^{238}U (mainly by conversion to plutonium). This correction may be calculat from the measured [Pu]/[^{238}U] ratio, and at low irradiations it will be small and t uncertainty negligible. At higher irradiations further corrections would be require for plutonium consumed by fission, but presumably these could also be calculated from the measured values of the $[Pu]/[^{238}U]$ ratio and the plutonium isotopic composition.

Possible application to accounting analyses in chemical processing plants

The procedure described appears to have many advantages if considered as a possible means of accountancy control in a chemical processing plant. For a solution containing a known mass of fuel elements a determination could take the following form. An aliquot of plant solution would be mixed with an aliquot of tracer. Neither aliquot need be measured accurately, for it is sufficient merely to ensure that the quantities mixed provide suitable $M_{239/242}$ and $M_{238/233}$ ratios for precise measurement in a mass spectrometer; an accuracy of say 20–30% would be adequate for each aliquot. Once mixed the method does not require a quantitative separation of either uranium or plutonium, for it is only necessary to ensure that the final specimens should contain sufficient material for a satisfactory mass spectral analysis. Thus a yield of 1–2% is adequate for uranium, and a minimum of perhaps 50% for plutonium. Under these conditions a single mass spectrometric analysis should provide a determination of the total plutonium content of the solution with a precision (1σ) of $\sim$0.3% together with uncertainties in the total quantity of uranium calculated from the mass of fuel elements.

In practice it would seem preferable to make dilutions and to take aliquots as accurately as possible. A single mass spectrometric analysis could then provide information for the following purposes: (*1*) a determination of the $[Pu]/[U]$ concentration ratio independent of plant sampling errors, (*2*) determinations of both plutonium and uranium concentrations with high analytical precision but also including sampling errors, (*3*) a determination of the plutonium isotopic composition from which the specific activity could be calculated with sufficient precision for radiochemical determinations.

At the present stage of development of mass spectrometers the method described would probably be too time-consuming to be applied at *frequent* intervals to a chemical plant. However, even in its present form it could provide a valuable supplement to existing methods. For example, one method of plant control is based on frequent radiochemical determinations of plutonium. These also require a knowledge of the specific activity of the plutonium, but this may be determined at less frequent intervals to give an average correction factor, either by a direct determination of the activity/mass ratio for the pure product, or by making a mass spectrometric analysis for a "bulked sample" of feed solution. In the latter case much would be gained by replacing this simple isotopic analysis by the procedure described in the present paper, for this would still provide the required specific activity determination, and in addition would give an independent and precise analysis for accountancy control. Sampling errors would be involved in preparing a "bulked aliquot", but for a plant operated on a batch basis this error would be small if the $[Pu]/[U]$ ratio did not vary greatly from batch to batch. Additional uncertainties may be introduced in a plant operated on a continuous basis, but errors associated with proportional sampling devices are outside the scope of this paper.

DETERMINATION OF ^{235}U IN ENRICHED URANIUM FUEL ELEMENTS

In view of the apparent advantages of employing a ratio technique for the determination of plutonium in natural uranium fuel elements, it is natural to enquire whethe a similar procedure could be applied to the determination of ^{235}U in highly enriche uranium fuel elements. In this case there is no experimental work to present so onl a brief discussion will be given.

The problem may be considered in terms of the Dounreay Materials Testin Reactor chemical plant[5]. This is designed to process fuel elements of enriched uraniur (93% ^{235}U)–aluminium alloy which have been irradiated to an extent that 20% c the ^{235}U originally present has been consumed by fission or by neutron captur The requirements for plant accounting analyses are (*1*) a determination of the ^{235} content of the irradiated fuel elements to provide a "plant input figure" of fissil material, (*2*) a determination of the quantity of ^{235}U consumed in the reactor fc costing purposes.

A previous paper assessed the precision of the isotopic dilution method for th determination of ^{235}U, and indicated a value of ~0.3% (1σ) for a single determinatio made for an aliquot of dilute mock feed solution[2]. For a reactor of the Dido type charge of fuel elements contains ~2,500 g of ^{235}U[14], and this might be processed i a chemical plant in ten batches, each containing 250 g[5]. Thus to determine the quantit of ^{235}U remaining in a charge of fuel elements either an aliquot must be taken fro each batch and these combined to give a solution representative of the charge, or determination made for each batch. The precision of a single determination made fc the solution of combined aliquots would be ~0.3%, and the overall precision obtaine by making a single analysis for each of the ten batches would be ~0.1%. The quantit of ^{235}U consumed in the reactor is then obtained by difference between the abov quantity and that known to be present in a charge before irradiation, so the corre sponding errors will be 1.2% and 0.4% respectively.

The above precision values refer only to the mass spectrometric method, and c not include plant sampling errors. The latter could well be considerably larger tha the mass spectrometric error, and so will be especially significant in the determinatio of the quantity of ^{235}U consumed. However, in principle at least, these could b eliminated by a ratio procedure involving determinations of ^{235}U and a suitab fission product. The use of a radioactive fission product to determine the quantit of ^{235}U consumed may not be acceptable, for corrections will be required for its deca and an accurate knowledge of the reactor irradiation time and subsequent "cooling time may not be available. However, this criticism would not apply to the use of stable fission product provided the precursors are of short half-life.

Assuming that an acceptable stable fission product nuclide (denoted by ^{i}F) ca be chosen, a ratio procedure could take the following form.

The concentration of ^{235}U in a plant solution may be obtained using eqn. (8) whe R(U) represents a function of the isotopic ratios determined by mass spectrometr for uranium; definitions of other symbols used are analogous to those used for eqn. (1

$$[^{235}\mathrm{U}]_s = [^{233}\mathrm{U}]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot R(\mathrm{U}) \cdot \frac{235}{233} \cdot D \qquad ($$

Similarly the concentration of the selected fission product nuclide ^{i}F may be d termined by mixing it with an aliquot of a tracer enriched in isotope i:

$$[^{j}F]_s = [^{i}F]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot R(\text{F.P.}) \cdot \frac{W_j}{W_i} \cdot D \tag{9}$$

where R(F.P.) represents a function of the various isotopic ratios determined for the fission product element; W_j and W_i are the atomic weights of isotopes j and i. Combining eqns. (8) and (9) gives:

$$\frac{[^{j}F]_s}{[^{235}\text{U}]_s} = C \cdot \frac{R(\text{F.P.})}{R(\text{U})} \tag{10}$$

where C is the product of a numerical constant and a concentration ratio determined for the tracer by calibration. Eqn. (10) is analogous to eqn. (3) and does not involve a knowledge of the mass of aliquots of sample or tracer, or of dilution factors. If a symbol k is now used to define the ratio of the number of atoms of ^{235}U destroyed, both by fission and by neutron capture, to the number of atoms of the selected fission product nuclide produced, eqn. (10) may be modified to give:

$$\frac{\text{U}_c}{\text{U}_r} = \frac{k.C.\ R(\text{F.P.})}{R(\text{U})} \tag{11}$$

where U_c is the quantity of ^{235}U consumed in the reactor, and U_r is the quantity remaining after irradiation. In practice small corrections will be required for the quantity of ^{235}U produced from ^{234}U, and for fission products derived from ^{238}U and ^{239}Pu. If the quantity of ^{235}U in a charge of fuel elements before irradiation is denoted by U_I, U_r and U_c may then be obtained as follows:

$$\text{U}_r = \text{U}_I \cdot \frac{1}{1 + k.C.\dfrac{R(\text{F.P.})}{R(\text{U})}} \tag{12}$$

$$\text{U}_c = \text{U}_I \cdot \frac{k.C.\dfrac{R(\text{F.P.})}{R(\text{U})}}{1 + k.C.\dfrac{R(\text{F.P.})}{R(\text{U})}} \tag{13}$$

In eqns. (12) and (13) the effect of uncertainties in the determination of plant solution volumes, dilution factors, etc., is completely eliminated, but unless the quantity of ^{235}U originally present in each batch is known and "plant hold-up" is negligible, this would be strictly true only if a complete charge of fuel elements could be dissolved altogether and a single representative sample taken. In practice volume and dilution data will be involved either in the preparation of a bulked sample typical of the ten batches, or in the calculation of the overall R(F.P.)/R(U) ratio from ten individual determinations, but unless the [selected fission product]/[^{235}U] ratio varies widely between batches, the uncertainty introduced by plant sampling errors in this way will be small.

If the ^{235}U usage is of the order of 20%, the expression $k.C.\ R$(F.P.)/R(U) will have a value of ~0.25, so if the percentage error in this expression is x the corresponding errors introduced into U_r and U_c will be 0.2 x and 0.8 x respectively. Thus, compared with the direct determinations outlined earlier, in the ratio procedure the significanc of experimental errors is reduced by a factor of 5 both for the determination of th quantity consumed and for the determination of the plant input figure.

In eqns. (12) and (13) the term C is obtained by a mass spectrometric calibratio of the mixed tracer, so uncertainties are introduced only by the random errors i the isotopic analyses and by those in the preparation of a mixed standard of ^{235} and the natural element form of the fission product; the term R(F.P.)/R(U) involve only isotopic ratios determined by mass spectrometry. These quantities are analogou to the first two terms of eqn. (3), and under favourable conditions a precision approaching that of the $[\text{Pu}]_s[\text{U}]_s$ ratio determinations should be achieved. An additiona uncertainty, however, is introduced by the term k relating the number of ^{235}U atom destroyed to the number of atoms of the chosen fission product nuclide, for there is bot the random error in the determination of k, and the question of whether it varies wit irradiation conditions, etc. This, in fact, is the quantity controlling the feasibilit or otherwise of the method. The following is not intended to be a complete discussio of this problem, but it is clear that the fission product nuclide selected must at leas satisfy the following conditions: (*a*) the variation of k with neutron energy should b a minimum, (*b*) its neutron cross section should be small, (*c*) its precursors should hav short half-lives, (*d*) there should be no segregation of the fission product elemen from uranium in the dissolver tank of the chemical plant, (*e*) subsequently th separation of the fission product element from uranium in the chemical plant shoul be sufficient to prevent errors arising from the use of recycled material, and (*f*) th element should be amenable to a mass spectrometric analysis, and a suitable trac should be available.

It is likely that no one fission product element will be wholly satisfactory. Howeve the basis of a determination need not be restricted to one element, for by using bot side filaments in the ion source it is quite feasible to determine both uranium an several fission products[15] in a single mass spectrometric analysis. A determinatio could then take the following form. It would be based primarily on the accura determination of a fission product chosen for minimum variation of k with neutro spectrum. For a given fission product element probably more than one isotope cou be used independently, and for preference the determination would be based on tw elements chosen to be close to each of the peaks of the thermal fission yield/ma number curve. If the variation of k between charges of fuel elements is found to b significant, then given a precise determination of a fission product for which k vari over a relatively small range, the selection of the appropriate value of k might b based on the determination of the relative quantity of a third fission product elemen having the maximum variation of k with neutron spectrum, chosen, for exampl to be close to the minimum of the thermal fission yield/mass number curve. In th way several independent values of R(F.P.)/R(U) and the appropriate value of k migh be obtained through a single mass spectrometric analysis.

One difficulty in the proposed scheme is that the quantity of feed solution requirin treatment would be much greater than that involved in a direct determination ^{235}U. A direct determination requiring $\sim$2 μg ^{235}U involves only $\sim$0.4 mC of fissio product activity, whereas a portion of solution containing $\sim$1 μg of an element c either maximum of the fission yield curve would contain $\sim$40 mC of activity, s handling problems would be rather more severe. The concentration of a fission produ uclide in the minimum of the fission yield curve would be lower by a factor of the rder of 100, so in this case the choice of element is essentially restricted to one having high sensitivity in a mass spectrometer. ^{115}In is a possibility; it has the disadvantage f a long-lived precursor (^{115}Cd, 43 d), but the yield of this is much lower than that f its shorter lived isomer (^{115}Cd, 54 h)[16], so this uncertainty might be acceptable in he calculation of a correction.

Given a suitable fission product, or combination of fission products, a single mass pectrometric analysis could provide information for the following purposes: (*1*) a letermination of the quantity of ^{235}U consumed in the reactor; this would be nearly ndependent of plant sampling errors, and the effect of random errors in the mass pectrometric analyses would be diminished by a factor of 1.25; (*2*) a determination f the ^{235}U input to a chemical plant; again this would be nearly independent of ampling errors, and the significance of random errors in the mass analyses reduced y a factor of 5; (*3*) a determination of the ^{235}U concentration in the plant feed solution but including sampling errors; (*4*) an isotopic analysis of the plant uranium by correction for the presence of the various tracer isotopes) to provide the mass ercentage of ^{235}U and the equivalent weight of the uranium for use with other anaytical methods.

CONCLUSIONS

The use of a ratio procedure for the analyses of feed solutions made in chemical rocessing plants for accountancy purposes offers several powerful advantages. Thus lant sampling errors are nearly eliminated and this enables high precision techniques o be exploited. The data presented show that for solutions of natural uranium fuel lements the [Pu]/[U] ratio could be determined with a precision (1σ) of $\sim$0.3% by single mass spectrometric analysis. The samples used in this work contained $\not> 0.01\%$ ^{242}Pu; in practice the ^{242}Pu content would increase with irradiation time, ut it can be shown that the ^{242}Pu correction will usually be very small for an irraliation of $\sim$1000 MWD/tonne, and that by calculating this correction it should be ossible to extend the method to solutions obtained even after irradiations of 5–6,000 IWD/tonne.

In principle a similar procedure might be applied in a chemical plant processing uel elements containing highly enriched ^{235}U. In this case both the quantity conumed in the reactor and the input figure for the chemical plant would be related to [stable fission product]/[^{235}U] ratio. The method is less fundamental than a direct letermination of ^{235}U and includes the uncertainty in the variation of the ratio atoms ^{235}U destroyed)/(atoms fission product nuclide produced) with neutron pectrum, but this disadvantage might be outweighed by the near elimination of lant sampling errors, and the five-fold reduction in significance of instrumental rrors in the determination of both of the required quantities.

The chief limitation of the mass spectrometric procedure is the time-factor. The Pu]/[U] ratio determinations were made at the rate of only one per day. This could e raised to two per day, but considerable time is also required for the actual measureent of the various ratios after they have been recorded, for each complete mass pectrometric analysis involved over 100 estimates of isotopic ratios. The method ould obviously be made even more attractive by instrumental developments peritting mass spectra to be both recorded and measured more rapidly.

APPENDIX I

ERRORS INVOLVED IN THE CALCULATION OF THE CONCENTRATION OF TOTAL PLUTONIU FROM A SINGLE MASS SPECTROMETRIC ANALYSIS

The expression for the concentration of total plutonium (eqn. 1) includes the following term:

$$\frac{M_{239/242} - T_{239/242}}{(\text{mass percentage } {}^{239}\text{Pu})_s} \qquad \text{(1}$$

or expressing "mass percentage" in terms of the ratios $S_{240/239}$ and $S_{241/239}$:

$$(M_{239/242} - T_{239/242}) \left(1 + \frac{240}{239} S_{240/239} + \frac{241}{239} S_{241/239}\right) \qquad \text{(1}$$

Expression (15) will apply directly when the determinations of $M_{239/242}$ and the iso topic composition of the sample are independent (*i.e.* based on separate mass spectro metric analyses). When these two quantities are determined by the same mas analysis the ratios $S_{240/239}$ and $S_{241/239}$ are not measured directly, but are calculate from the observed mixture and tracer ratios, so the precision for the determinatio of these two terms will usually be worse than that obtained by a direct analysi Thus the *apparent* increase in error when a determination of the concentration of tot plutonium is based on a single mass spectrometric analysis, instead of on separa analyses for $M_{239/242}$ and the isotopic composition, will arise from the increase in the e ror due to the second part of expression (15). Typical values of the ratios and of coe ficients of variation for direct determinations and for values calculated from mixtu analyses respectively are: $S_{240/239}$, 0.040 (0.25%, 2%); $S_{241/239}$, 0.0024 (1%, 15%); th corresponding errors for the second part of expression (15) are then 0.01% and 0.09

In basing a determination of the concentration of total plutonium on a single ma spectrometric analysis the error component arising from the determination of th isotopes ^{240}Pu and ^{241}Pu will therefore increase, but in fact this will be offset to som extent by a small decrease in the significance of the error in the measurement of th ratio $M_{239/242}$. Thus if eqns. (5) and (6) are used to express $S_{240/239}$ and $S_{241/239}$ sole in terms of mixture and tracer ratios, expression (15) becomes:

$$(M_{239/242} - T_{239/242}) + \frac{240}{239}(M_{240/242} - T_{240/242}) + \frac{241}{239}(M_{241/242} - T_{241/242}) \qquad \text{(1}$$

Then if the percentage error in $M_{239/242}$ is $\triangle M$, the errors introduced by this in expressions (15) and (16) will be

$$\frac{M_{239/242}}{M_{239/242} - T_{239/242}} \cdot \triangle M \qquad \text{(1}$$

and

$$\frac{M_{239/242}}{(M_{239/242} - T_{239/242}) + \frac{240}{239}(M_{240/242} - T_{240/242}) + \frac{241}{239}(M_{241/242} - T_{241/242})} \cdot \triangle M \qquad \text{(1}$$

respectively. Typical values of the various ratios are $M_{239/242}$, 1; $M_{240/242}$, 0.045; $M_{241/242}$, 0.005; $T_{239/242}$, 0.005; $T_{240/242}$, 0.005; $T_{241/242}$, 0.002_3; substituting these gives a value of 0.96 for the ratio of expression (18) to expression (17).

Assuming a value of 0.20% for the coefficient of variation for the factor ($M_{239/242} - T_{239/242}$), then when the ratio $M_{239/242}$ and the isotopic composition of the plutonium are determined by separate mass spectrometric analyses, the errors to be combined are 0.20% and 0.01%, and the coefficient of variation for expression 15 is $0.20_0\%$. When the two quantities are determined by a single mass spectrometric analysis the errors to be combined are $0.96 \times 0.20\%$ and 0.09%, so the overall error for expression (16) is $0.21_2\%$. (For comparison a direct combination of errors of magnitude 0.20% and 0.09% would give an overall value of $0.21_9\%$).

The above account is incomplete for the error in the factor ($M_{239/242} - T_{239/242}$) will usually be less than 0.20%, and some other error components (calibration of tracer, uncertainty in mass of aliquots of sample and tracer, etc.) will be common to both types of determination. However, it illustrates that relatively little should be lost in basing a determination on a single mass spectrometric analysis. For material produced after longer irradiations, the relative quantities of ^{240}Pu and ^{241}Pu will be larger. The disparity between the two methods of estimating ^{240}Pu and ^{241}Pu should then decrease, and further the value of the coefficient of $\triangle M$ in expression (18) will also decrease. Thus the single analysis method should continue to be attractive until the growth of ^{242}Pu becomes the limiting factor.

APPENDIX 2

GROWTH OF ^{242}Pu WITH IRRADIATION TIME

The procedure described in "Determination of plutonium in natural uranium fuel elements" involves the assumption that the ^{242}Pu content of the samples is negligible. This may be acceptable for uranium irradiated to the extent of perhaps 1,000 MWD/tonne, but at higher irradiations the ^{242}Pu content will increase and will require consideration. However, even when the ^{242}Pu content is significant, if it is small it may still be possible to make a determination by one mass spectral analysis. For a given reactor and operating procedure the variation of plutonium isotopic composition with irradiation might be found either by calculation or by experiment. Using these data curves may be constructed showing the variation of the ^{242}Pu/^{239}Pu ratio with both the ^{240}Pu/^{239}Pu ratio and the ^{241}Pu/^{239}Pu ratio. For any given sample the measured ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios (*i.e.* calculated from measured mixture and tracer ratios) may each be used with the curves to find the appropriate ^{242}Pu/^{239}Pu ratio, which is then used in the calculation of the total quantity of plutonium. In order to illustrate the errors introduced by such a procedure the data quoted for a typical natural uranium graphite moderated power reactor have been taken as an example of the variation of plutonium isotopic composition[11], and used in the calculations below. In practice, for a given reactor operated at a fairly constant irradiation level, calibration curves might be constructed from a few "unspiked isotopic analyses" for the plant solutions.

Eqns. (5) and (6) enable the $S_{240/239}$ and $S_{241/239}$ ratios to be calculated from mixture and tracer ratios when the sample contains a negligible quantity of ^{242}Pu. If, however, the ratio $S_{242/239}$ has a finite value, the equations take the following modified form:

$$S_{240/239} = \frac{M_{240/242} - T_{240/242}}{M_{239/242} - T_{239/242}} + \frac{M_{239/242} \cdot T_{240/242} - M_{240/242} \cdot T_{239/242}}{M_{239/242} - T_{239/242}} \cdot S_{242/239} \qquad \text{(19}$$

$$S_{241/239} = \frac{M_{241/242} - T_{241/242}}{M_{239/242} - T_{239/242}} + \frac{M_{239/242} \cdot T_{241/242} - M_{241/242} \cdot T_{239/242}}{M_{239/242} - T_{239/242}} \cdot S_{242/239} \qquad \text{(20}$$

Eqn. (1) also becomes:

$$[\mathrm{Pu}]_s = [{}^{242}\mathrm{Pu}]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{D}{242} \cdot \frac{M_{239/242} - T_{239/242}}{1 - M_{239/242} \cdot S_{242/239}} \cdot (239 + 240\, S_{240/239} + 241\, S_{241/239} + 242\, S_{242/239}) \qquad \text{(21}$$

Eqn. (19) may be considered in two parts: the first term which is analogous to eqn (5), and a second term involving $S_{242/239}$, the $^{242}Pu/^{239}Pu$ ratio for the sample. Assuming a value of unity for the $M_{239/242}$ ratio throughout, the relative values of these terms may be calculated for various irradiation levels. In this way it may be shown that the contribution of the second term is very small, both for $S_{240/239}$ and $S_{241/239}$ increasing from ~0.01% at 2,000 MWD/tonne to ~0.05% at 8,000 MWD/tonne. Thu the errors introduced in applying these corrections will be negligible, and it is justifie to use the calculated values of $S_{240/239}$ and $S_{241/239}$ to find $S_{242/239}$.

By using the calibration plots (based in this case on reference[11]) the errors in th $^{242}Pu/^{239}Pu$ ratio corresponding to error values assumed for the $^{240}Pu/^{239}Pu$ an $^{241}Pu/^{239}Pu$ ratios may also be found, and then, using eqn. (21), the equivalent erro for the total quantity of plutonium. This procedure has been used to calculate th values listed in Table V, where it has been assumed that $S_{240/239}$ and $S_{241/239}$ ar determined to ±0.0005 for values of 0.05 or less, and to 1% for values greater tha 0.05, and also that a $M_{239/242}$ ratio of ~1 is used throughout.

TABLE V

ERRORS IN $[Pu]_s$ EQUIVALENT TO ERRORS IN $^{240}Pu/^{239}Pu$ AND $^{241}Pu/^{239}Pu$ RATIOS WHEN USED T CALCULATE THE ^{242}Pu CORRECTION

Irradiation level MWD/tonne	*Error using $^{240}Pu/^{239}Pu$ ratio* %	*Error using $^{241}Pu/^{239}Pu$ ratio* %
2000	~0.01	~0.03
3000	0.04	0.02
4000	0.08	0.04
5000	0.13	0.07
6000	0.2	0.11
8000	0.5	0.2

The later entries in the second column are probably overestimates for as th $^{240}Pu/^{239}Pu$ ratio reaches 0.2–0.4 it will be determined with a better precision tha 1%. It therefore seems that if necessary this interpolation procedure could be use without introducing serious errors, up to an irradiation of 5–6,000 MWD/tonne. similar calculation based on isotopic data for N.R.X.[12,13,17] combined with ^{242}P production rates calculated for M.T.R. Idaho[18] also gives results which are comparab (slightly smaller) with the errors listed in Table V.

SUMMARY

A procedure is described for the determination of the [total Pu]/[total U] concentration ratio for a given solution by an isotopic dilution method. Results obtained for two samples give a mean precision (1σ) of 0.3% for a determination made by a single mass spectrometric analysis. A possible application of the method would be its use for plutonium accounting analyses in a chemical plant processing natural uranium fuel elements, an important feature being the near elimination of the effect of plant sampling errors. An outline is also given of a similar procedure which might be used for the determination of ^{235}U in a plant processing enriched uranium–aluminium alloy reactor fuel.

RÉSUMÉ

Une méthode par dilution isotopique est décrite pour la détermination du rapport de concentrations [Pu total]/[U total] dans une solution donnée. Une application de ce procédé est possible dans les installations utilisant l'uranium naturel comme combustible.

ZUSAMMENFASSUNG

Beschreibung einer Isotopenverdünnungsmethode zur Bestimmung des Konzentrationsverhältnisses [total Pu]/[total U] in einer Lösung. Es wurde bei zwei Substanzproben durch eine Massenspektrometrische Analyse eine mittlere Präzision von 0.3% erzielt. Mögliche Anwendungen der Methode in uran-verarbeitenden Betrieben werden erwähnt.

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RADIOCHEMICAL SEPARATION OF COBALT*

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INTRODUCTION

The separation of cobalt-60 from other radio-isotopes emitting hard γ-rays is of grea importance, *e.g.* in activation analysis**. In many irradiated samples (blood, steel etc.) especially iron-59 and zinc-65 are present in large excess over the cobalt-60

The methods suggested for the separation of cobalt-60 include paper chromato graphic, ion-exchange, precipitation and extraction techniques[2–6]; but with a large excess of iron-59 or zinc-65 we found that none of these methods was quite satis factory.

PŘIBIL *et al.*[7] made use of the extraordinary stability of the cobalt diethyldithio carbamate complex for the selective colorimetric determination of microgram amount of cobalt. The complex was extracted into chloroform and all other colored diethyl dithiocarbamate complexes were decomposed by shaking with an aqueous solutio of mercury(II).

The same reactions were applied by the present author for the radiometric determi nation of submicrogram amounts of cobalt, using either diethyldithiocarbamate-^{35} or mercury-203 (in contradistinction to microgram amounts of cobalt, extraction wit diethyldithiocarbamate at pH 14 was incomplete)[8].

In the present work cobalt and other carriers were added to the irradiated sampl and extraction of the cobalt complex was carried out at pH 14. The treatment wit mercury(II) was unnecessary, because iron-59 and zinc-65 were co-extracted only t the extents of 0.0005 and 0.04% respectively.

PROCEDURE

After the irradiation add metal-carriers in 100 μg*** amounts, ash and/or dissolve i mineral acid and, if necessary, separate the heavy metals by precipitation as th hydroxides.

Dissolve in a few ml of 1 *N* hydrochloric acid and place the solution in a tightl lidded P.V.C. pill-capsule of diameter 25 mm and height 76 mm.

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* Publication No. 134 of the Research Institute for Animal Husbandry, "Schoonoord", Hoogt 10bis Utrecht (The Netherlands).

** KAISER AND MEINKE[1] carried out the neutron activation analysis of cobalt, using the *sof* γ-radiation of cobalt-60m ($\tau_{\frac{1}{2}} = 10.5$ min).

*** Alternatively 1 mg of each metal is added as a carrier; in this case 0.05 *M* tartrate and 1 mg of diethyldithiocarbamate are used.

Dilute to 5 ml, add some phenolphthalein and add potassium sodium tartrate up to 0.01 M*. Neutralise with alkali, add an excess of 0.6 ml of 10 N sodium hydroxide and then 1 mg of diethyldithiocarbamate*.

Shake mechanically** with 5 ml of carbon tetrachloride (AnalaR), centrifuge lightly to remove drops from the upper walls and remove the upper layer with a pipette. Rinse by shaking with alkaline tartrate, dry the carbon-tetrachloride layer by filtration (*e.g.* through a SS-595 paper) and evaporate by a stream of nitrogen to the volume of the well-type counter. Measure the radio-activity of cobalt-60 by scintillation counting*** and the amount of the cobalt complex with a spectrophotometer (4000 Å).

The time required for a determination in duplicate is 40 min; the efficiency for cobalt is about 50%.

DISCUSSION

The results (Table I) show that less than 0.0005 and 0.04% of iron and zinc respectively are extracted. About 0.05% of the activity of both pile- and cyclotron-produced

TABLE I

EXTRACTION OF IRON-59 AND ZINC-65 BY DIETHYLDITHIOCARBAMATE AT pH 14[a]

^{59}Fe	*Pile*[b]	*Cyclotron*[c]
1 Freshly irradiated	40	48
2 After 70 days (1.5 times $\tau_{\frac{1}{2}}$)	105	185
3 As no. 2; purified[d]	<0.5	<3
4 As no. 2; no Co-carrier[e]	<0.5	<0.5
^{65}Zn	*Pile*	
1 Non-purified	35	
2 Purified[f]	40	

[a] Tracer is added to give an original count-rate of 10^5 C/min; mean values of 4 experiments are given in C/min found in the final organic layer.

[b] ^{59}Fe was produced by the ^{58}Fe(n,γ) ^{59}Fe reaction; some ^{60}Co was formed (by (n,γ) reactions) from the small amounts of cobalt in the iron target. (Amersham – UK)

[c] ^{59}Fe was produced by the ^{59}Co (d, 2p)–^{59}Fe reaction (in concurrence with the ^{59}Co (d,p)–^{60}Co reaction) from a cobalt-target. Most of the ^{60}Co was removed by the manufacturer (Philips-Duphar, Amsterdam).

[d] Purified — after the addition of Fe- and Co-carriers — by N successive extractions with isopropylether from 7 N HCl, evaporation of the ether, addition of new carriers and HCl up to 7 N, and repetition (M-times) of the process. In column 2: N = 2 and M = 3, the efficiency for Fe and Co was 80 and 0.02% respectively In column 3: N = 3 and M = 2, and the respective efficiencies were 95 and 1%.

[e] Carrier-free cobalt is extracted very incompletely (see introduction).

[f] ^{65}Zn was purified by descending paper chromatography. The solvent (acetone–4 N HCl = 75 : 25) was allowed to drip off.

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* Alternatively 1 mg of each metal is added as a carrier; in this case 0.05 M tartrate and 10 mg of diethyldithiocarbamate are used.

** Shaking was carried out in a vertical position in the "Microid flask shaker" at 900 periods per min for 3 min.

*** A Philips detector (PW 4111 W) and scaler (PW 4022-4032-4052), combined with an E.K.A.F. single channel analyser (30301–20102), were used.

iron-59 is due to cobalt-60. (For the pile-produced iron-59 the manufacturer gave the value: <0.1 %).

When the alkaline back-extraction is omitted or when it is replaced by a simple rinsing, results with iron-59 are 5 to 30 times higher. When the procedure is carried out with 1 ml of both layers, evaporation of the organic layer is not required but results with iron-59 are doubled.

Addition of the diethyldithiocarbamate reagent at lower pH values results in higher extraction percentages of iron-59. The addition of ammonium tartrate, sodium fluoride, pyrophosphate, "tiron", or ascorbic acid does not have any favourable influence on the results. The use of 10 mg of each carrier in the 5-ml volume resulted in precipitation. The addition of mercury(II) or potassium cyanide to the alkaline tartrate used for the back-extraction did not improve the results.

ACKNOWLEDGEMENTS

The authors' thanks are due to Miss J. H. F. F. BROEKMAN for valuable technical assistance.

SUMMARY

A method is described for the radiochemical separation of cobalt based on the extraordinary stability of cobalt diethyldithiocarbamate. Interferences are few; only very small amounts of zinc and iron accompany cobalt, which is important in neutron-activation analysis.

RÉSUMÉ

Une méthode est proposée pour la séparation radiochimique du cobalt, sous forme de diéthyldithiocarbamate; ce composé présente une stabilité remarquable.

ZUSAMMENFASSUNG

Es wird eine radiochemische Abtrennungsmethode für Kobalt beschrieben. Sie beruht auf der aussergewöhnlichen Stabilität des Kobalt–Diäthyl-dithiocarbamat Komplexes.

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SOME REMARKS ABOUT THE USE OF THE BOMB CALORIMETER

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For respiration experiments with cows, in which it is important to establish the energy balances, we had to determine the calorific value of many samples of feeding stuffs, faeces, urine, etc. These values were measured in a bomb calorimeter by determining the rise of temperature in the inner calorimeter vessel, keeping the water in the outer vessel at a constant temperature. For these experiments it is sufficient to attain an accuracy of 0.2–0.3%.

The experience obtained in this work gives rise to some remarks which may be useful to other workers in this field.

The accuracy of the thermometer

Usually in calorimetry a thermometer is used with a scale graduated to 0.01°, whilst readings are estimated to 0.001°. However, in verifying thermometers of this kind the accuracy is about 0.01° and certainly not 0.001° (private communication from Van der Waals Laboratory, Amsterdam). It is our opinion that, even in legally verified thermometers, both the initial and final temperature may be 0.005° in error, so that in unfavourable circumstances the maximum error will amount to about 0.01°. This means a relative error of about 0.5%, if the total temperature rise is about 2°. In the usual method of determining the combustion value this thermometer error undoubtedly provides the limiting factor.

In order to reduce the unfavourable influence of unknown thermometer errors our method was modified so that in all determinations nearly the same section of the thermometer could be used (see also Coops *et al.*[1]). For our calorimetric determinations the initial temperature is always the same, being chosen as 19.0° (between 19.00 and 19.04). Furthermore so much material is burnt in the bomb that the temperature rise is between 1.6° and 1.9°. Thus, our end-temperatures are always between 20.6° and 20.9°. This range from 1.6° to 1.9° could be reduced if necessary; in fact nearly all temperature rises are between 1.7 and 1.8°. This method of measuring reduces considerably the influence of unknown thermometer errors. Since in calorimetric work the determinations are based on the known calorific value of substances such as benzoic acid, succinic acid, etc., it is not important to know the absolute temperature rise. As a matter of fact in our case thermometer errors from 19.0° to 20.6° are immaterial, so that it is enough to establish possible irregularities in the range 20.6°–

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* Director: Prof. Dr. E. Brouwer.

20.9°; the irregularities over such a small interval will usually be negligible. Moreover the section of the thermometer between 20.6 and 20.9 can be verified accurately wit benzoic acid in the following manner. With different amounts of benzoic acid th water value of the calorimeter is determined. The amounts of benzoic acid are chose so that the final temperatures are successively about 20.6, 20.7, 20.8 and 20.9°. If th water values corresponding to the different final temperatures are in good agreement no thermometer corrections have to be applied. If the water values found over th range 20.6–20.9 do not agree sufficiently, a certain point in the region 20.6–20.9, fo instance 20.6, is assumed to be correct and for the other points of the region suc thermometer corrections are applied that the calculated water values correspond t the water value at the chosen point 20.6.

With a material such as benzoic acid (homogeneous and nonhygroscopic) the wate value, if determined in duplicate, can be established with an accuracy of about part in 1000 (0.1%). This means that in verifying the thermometer with benzoi acid as described, an accuracy can be obtained of 0.1% of the total rise (± 1.8°) *i.e.* about 0.002°.

In order to be able to start the measurements at the fixed temperature of 19° we placed a simple electric heater (40 V, 50 Watt) in the inner calorimeter vesse At the beginning of every determination the inner calorimeter vessel is filled wit water, the temperature of which is somewhat less than 19°; the water is then warme with the electric heater to nearly 19.0° and stirred for 10 min to ensure that equilib rium is established. In the outer vessel (water jacket) are placed an electric heate (220 V, 350 Watt) and a spiral copper tube for cooling with tap water. Mixing of th water in the outer vessel can simply be achieved by forcing air through the wate with a rubber bulb. Thus the temperature of the outer vessel can also be adjuste at will, which is very important, for now one is always able to measure under standar conditions. The temperature of the outer vessel is chosen as about 0.5° lower than th expected final temperature in the inner vessel, thus, as a rule, the temperature i the outer vessel is 20.2° or 20.3°.

The measures mentioned above proved to ensure more reliable and more accurat results and, in our opinion, it would be desirable for calorimeters to be built so tha the temperatures in the outer and inner vessels can be regulated.

A simple, accurate correction-formula

The temperature rise measured after the firing must be corrected because this ris is influenced by the differences between the temperatures of the inner and oute vessels. The best approximation of this correction is given by the theoretically derive formula of REGNAULT–PFAUNDLER[2], which can be written as follows:

$$c = \frac{V_1 - V_2}{R}\left(T_1 + T_2 + \ldots\ldots\ldots T_{n-1} + \frac{T_0 + T_n}{2} - n\,T_0\right) - n\,V_1$$

where V_1 and V_2 = temperature rise per time interval (30 sec) in the initial and fina periods respectively, $T_0, T_1 \ldots T_n$ = temperature readings in the combustion perio R = temperature rise in the combustion period and n = number of time interva (30 sec) in the combustion period.

The use of this formula involves a rather time-consuming calculation with ever determination. However, for every calorimeter and bomb it is quite easy to deriv from the mentioned formula a very simple one, which is almost as accurate as the REGNAULT–PFAUNDLER formula. From a large number of observations it turned out that the temperature rise after the firing, if plotted graphically, always follows the same type of curve, practically independently of the kind of material burnt. The shape of the temperature–time curve is mainly determined by the material of the bomb and the construction of the apparatus. After the first time interval (30 sec) in the combustion period the rise is a certain fraction of the total rise ($T_1 = T_0 + \alpha_1 R$), and also after the second, third, etc. intervals ($T_2 = T_0 + \alpha_2 R$; $T_3 = T_0 + \alpha_3 R$; etc.). For the equation of REGNAULT–PFAUNDLER we now can write:

$$c = \frac{V_1 - V_2}{R} \left\{ n\,T_0 + (\alpha_1 + \alpha_2 + \ldots \alpha_{n-1} + \frac{\alpha_n}{2} (R - n\,T_0 \right\} - n\,V_1$$

or:

$$c = (V_1 - V_2)\,(\alpha_1 + \alpha_2 \ldots \alpha_{n-1} + \frac{\alpha_n}{2}) - n\,V_1$$

For our calorimeter and two old bombs (old-type bombs, manufacturer Julius Peters, Berlin) the combustion period is 5 min and we always use time intervals of 30 sec, therefore $n = 10$. For the calculation of $\alpha_1 + \alpha_2 + \ldots \alpha_{n-1} + \frac{1}{2}\alpha_n$ we used the readings of 48 determinations (hay, dried faeces, urine dried on cellulose, benzoic acid). The mean value of this sum proved to be 8.75 with a standard deviation of 0.06. Thus, for our calorimeter with old bombs the formula could be changed into:

$$c = (V_1 - V_2)\,8.75 - 10\,V_1 = -8.75\,V_2 - 1.25\,V_1$$

The algebraic signs of V must be carefully watched; a decrease of the temperature during the initial or the end period means that V is negative.

For our calorimeter with old bombs this very simple formula is nearly just as accurate as the original formula. The small fluctuations found for the sum $\alpha_1 + \alpha_2 +$ etc. (standard deviation 0.06) are mainly caused by the quick temperature rise in the first part of the combustion period, which entails inaccurate readings. These inaccurate readings also cause some uncertainty in using the formula of REGNAULT–PFAUNDLER.

For control the correction was calculated in both ways for 12 determinations. The results are given in Table I.

As can be seen, the differences between the pairs of corrections are negligible,

TABLE I

Organic matter	*I* *Simple formula*	*II* *Regnault –Pfaundler*	*I–II*
hay	—0.0042	—0.0042	0.0000
hay	—0.0021	—0.0021	0.0000
hay	—0.0011	—0.0009	—0.0002
hay	—0.0022	—0.0021	—0.0001
faeces	+0.0021	+0.0020	+0.0001
faeces	+0.0006	+0.0005	+0.0001
faeces	—0.0008	—0.0010	+0.0002
faeces	0.0000	—0.0001	+0.0001
flour	—0.0010	—0.0009	—0.0001
urine	—0.0004	—0.0003	—0.0001
urine	—0.0038	—0.0035	—0.0003
urine	—0.0031	—0.0030	—0.0001

especially if it is considered that the uncertainty in the readings and in the calibratio of the thermometer is many times larger. For every calorimeter and bomb a corresponding simple formula can be derived after a number of determinations has bee done. We found however that the difference between two bombs can be very larg in this respect. The example given above holds for our two old bombs from Juliu Peters, Berlin. For a newly received bomb (manufacturer also Julius Peters) it appeared that the heat exchange after the combustion was much slower than with th old bombs. Whilst the combustion period for the old bombs was only 5 min ($n = 10$) the combustion period for the new bomb appeared to be 9 min ($n = 18$). The correction formula for the new bomb proved to be: $c = -15.5\ V_2 - 2.5\ V_1$. The slow hea exchange of the new bomb can probably be attributed to a low heat conductivity o the material of the bomb and must be called an important disadvantage for tw reasons: the determinations are more time-consuming and the calculation of the correction is less accurate. For calorimetric bombs material of high heat conductivit is to be preferred.

SUMMARY

In order to reduce the unfavourable influence of unknown thermometer errors, the method fo the determination of the calorific value of organic matter in the calorimetric bomb is modifie so that in all determinations nearly the same section of the thermometer is used. For the correctio of the observed temperature rise a very simple formula is derived from the more elaborate formul of REGNAULT–PFAUNDLER.

RÉSUMÉ

L'auteur propose une modification de la détermination de la chaleur de combustion de substance organiques par la bombe calorimétrique, permettant d'éviter des erreurs dues au thermomètr Pour la correction, on utilise une formule de REGNAULT–PFAUNDLER simplifiée.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Eliminierung des Einflusses des Thermometerfehlers bei de Bestimmung des Kaloriengehaltes von organischem Material im Kalorimeter. Zur Korrektur wir eine vereinfachte Formel von REGNAULT–PFAUNDLER verwendet.

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DETERMINATION OF FORMIC ACID BY CATALYTIC OXIDATION WITH CERIUM(IV)

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Cerium(IV) has been used for the oxidative determination of organic compounds by several workers[1-4]. In most cases the oxidation proceeds to the formation of carbon dioxide, water, formic acid and higher fatty acids. Although it has been reported that formic acid is resistant to further oxidation, impurities present in the ceric salts may induce partial oxidation of formic acid; the reaction may thus be non-stoichiometric. This necessitates the use of empirical factors for the determination of certain compounds. In order to overcome this difficulty SHARMA AND MEHROTRA[2] suggested chromium sulphate as catalyst and a sulphuric acid concentration of 50–60%; formic acid is then oxidised by cerium(IV) to carbon dioxide. Other organic compounds which are normally oxidised to the formic acid stage by cerium(IV) are then also oxidised to the carbon dioxide stage and the reaction becomes more stoichiometric and better suited for quantitative work.

Under the conditions used by SHARMA AND MEHROTRA[2] there is always a danger of loss of volatile oxidation products .We therefore considered the possibility of using some catalyst in the presence of which formic acid can be oxidised at ordinary temperature. We have already described[4] a photochemical method for the oxidation of organic compounds at room temperature which eliminates the possibility of volatilisation of oxidation products.

Although SHARMA AND MEHROTRA did not discuss the mechanism of the catalytic action of chromic sulphate, it appears that chromium(III) is oxidised to the hexavalent state[5] which is re-reduced by formic acid. Among other oxidants used for the oxidation of formic acid, bromine reacts at ordinary temperatures[6], being reduced to hydrogen bromide. In presence of cerium(IV), bromine is regenerated and a chain reaction is set up which can be represented as follows:

$$2\,Br^- + 2\,Ce^{+4} \rightarrow Br_2 + 2\,Ce^{+3}$$
$$HCOOH + Br_2 \rightarrow 2\,HBr + CO_2$$

This reaction has been used as the basis for the oxidation of formic acid by cerium(IV) in the present investigation.

EXPERIMENTAL

Stock solutions of ceric salts were prepared by dissolving the requisite amount of ceric sulphate (A.R., B.D.H.) in sulphuric acid so that the final acidity was 1.0 N.

This solution was standardised iodimetrically[7] by running a blank as described below Since formic acid may contain some oxidisable impurities it was distilled from a solution containing 100 ml of 90% formic acid, 2 g of ceric sulphate and 20 ml of 4 N sulphuric acid. In the distillate formic acid was determined by reduction of mercuri chloride; finally, the solution was diluted to give a concentration of 0.02 *M*.

Oxidation of formic acid

To a known amount of formic acid solution in an iodine flask, excess of cerium(IV solution and 0.5–1.0 ml of 1% potassium bromide solution were added. The fina solution was made 2 *N* in sulphuric acid. After about an hour, excess of 10% potassium iodide solution was added and the liberated iodine was titrated with standard sodium thiosulphate solution. A blank determination was run simultaneously on the sam amounts of ceric sulphate and potassium bromide without formic acid. The differenc between the test and blank runs corresponds to the equivalents of cerium(IV) con sumed by the formic acid. Different amounts of formic acid and ceric sulphat solution were examined as indicated in Table I. The amount of potassium bromid was also varied; with insufficient concentrations of potassium bromide, the reactio time was longer while with high potassium bromide concentrations low results wer obtained owing to loss of bromine. The results are given in the Table I.

TABLE I

Volume of 0.02 M formic acid (ml)	*Volume of 0.05 M cerium(IV) solution (ml)*	*Volume of 1% potassium bromide solution (ml)*	*Time for completion of the reaction (min)*	*Volume of 0.05 M cerium(IV) solution consumed (ml)*
1.0	2.0	0.5	45	0.80
2.0	3.0	0.5	60	1.64
5.0	4.0	1.0	80	3.98
10.0	6.0	1.0	100	3.95

Further oxidation of the photochemical oxidation products of certain hydroxy acids wit cerium(IV)

The oxidation of malic, tartaric and citric acids were carried to the formic acid stag photochemically as described earlier[4]. To the oxidation products 1.0 ml of 1% potassium bromide solution was added and the solution was set aside for a certai time before the excess of cerium(IV) was determined iodimetrically. Thus these acid can be oxidised in two stages to carbon dioxide and water. Table II shows the result of oxidation of these acids.

TABLE II

Acid	*Volume of 0.02 M acid (ml)*	*Volume of 0.05 M cerium(IV) solution (ml)*	*Equivalents per mole consumed in photochemical oxidation*[4]	*Volume of 1% potassium bromide solution (ml)*	*Time for complete oxidation (min)*	*Total equivalent of oxygen per mole found*
Malic	1.0	10	8	1.0	100	11.98
Tartaric	1.0	10	6	1.0	100	10.00
Citric	1.0	20	14	1.0	120	18.08

DISCUSSION

It has been observed that formic acid can be oxidised stoichiometrically to carbon dioxide and water by cerium(IV) in presence of a small quantity of potassium bromide. The complete oxidation of those acids which are normally oxidised to the formic acid stage in absence of potassium bromide can also be brought about. In comparison to other procedures used for the oxidation of hydroxy acids by cerium(IV) where the oxidation does not proceed as far as the carbon dioxide stage, the present method has the advantage of yielding more definite products of oxidation. The method is preferable to that involving oxidation of formic acid by standard bromine or bromate–bromide solution because there is no possibility of bromine losses; bromine is generated in very low concentration and is immediately consumed. After the completion of the reaction an amount of bromine equivalent to the potassium bromide added remains in the solution and thus the oxidation may be considered to be brought about indirectly by cerium(IV). This bromine along with the unreacted cerium(IV) liberates an equivalent amount of iodine from potassium iodide. Hence the difference in the amount of iodine liberated by the solution containing formic acid and blank is equivalent to the amount of cerium(IV) used for the oxidation of formic acid. The method can also be used for the complete oxidation of those compounds which give formic acid as the product of oxidation with cerium(IV) under ordinary conditions. The method can also be applied to the complete oxidation of polyhydroxy alcohols and sugars, which will be described shortly.

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SUMMARY

A method is proposed for the determination of formic acid by oxidation with cerium(IV) in presence of potassium bromide. The method can also be used for the further oxidation of organic compounds which yield formic acid under ordinary conditions with cerium(IV).

RÉSUMÉ

Une méthode est proposée pour le dosage de l'acide formique, par oxydation au moyen de cérium (IV), en présence de bromure de potassium. Les auteurs envisagent également le dosage des acides malique, tartrique et citrique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Ameisensäure durch Oxydation mit Cerium(IV) n Gegenwart von Kaliumbromid. Die Methode kann auch zur Bestimmung von Äpfelsäure, Weinsäure und Citronensäure verwendet werden.

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A NEW RAPID SEMIMICRO TITRIMETRIC DETERMINATION OF MERCURY

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The determination of total mercury, especially in mg amounts, remains a difficu
problem. The direct titrimetric method for mercury by means of ammonium th
cyanate[1] is seriously affected by even small amounts of halide ions, which is a co
siderable drawback. A survey of the literature shows that although considerable wo
has been done on the determination of mercury in widely different materials, a gene
simple method applicable to most of its compounds, both inorganic or organic,
not yet available. ROBINSON[2] separated mercury by precipitation with hypopho
phorous acid and titrated it with iodine; in this determination, the conditions mu
be strictly controlled and the results obtained are rather low. Recently BROOKES A
SOLOMON[3] separated mercury from interfering substances by a distillation procedu
in which a fused-silica distillation flask is used; the metal was then dissolved in nit
acid and titrated with ammonium thiocyanate solution. The results obtained we
comparatively low for small amounts of mercury. The present paper describes
systematic investigation of a simple titrimetric method which is applicable to
wide range of compounds and preparations containing small amounts of mercu
and is relatively free from interferences.

This method, by which small amounts of mercuric ions (0.5 to 5.0 mg) can
determined accurately, is based on titration with potassium iodide solution in preser
of sodium bicarbonate; potassium periodate is used as indicator. The reactions a

$$Hg^{+2} + 2I^- \rightarrow HgI_2$$

$$IO_4^- + 2I^- + H_2O \rightarrow IO_3^- + I_2 + 2OH^-$$

The end-point of reaction (1) is indicated by the colour imparted by iodine (2)
carbon tetrachloride previously added to the mixture. A small amount of potassiu
or sodium chloride is added to the test solution to prevent the precipitation of m
curic periodate.

EXPERIMENTAL

Mercuric chloride solutions were prepared by weighing accurately small amounts
the chemically pure (A.R.) salt and dissolving them in water.

Procedure for titrating mercury

An aliquot of the mercuric chloride solution containing 0.5 to 5.0 mg of Hg was placed in a glass-stoppered 150 ml conical flask and diluted to about 80 ml with distilled water. Potassium chloride (*ca.* 0.1 g) was added. (This is not necessary if the sample solution is prepared with aqua regia or hydrochloric acid). If necessary, the solution was neutralised cautiously with sodium bicarbonate. Sodium bicarbonate (5 g) was then added followed by 5 ml of a saturated solution of potassium metaperiodate and 3 ml of pure carbon tetrachloride. The volume of the solution was then diluted to approximately 100 ml with water and titrated with 0.01 *N* potassium iodide solution added dropwise at a rate of about one drop per second from a microburette. Towards the end of the titration the solution was shaken for 5–10 sec between each addition. The end-point was indicated by the appearance of the free iodine colour in the organic layer. A blank test was always carried out under the same conditions. One ml of 0.01 *N* potassium iodide is equivalent to 1.003 mg of mercury. The results are shown in Table I.

TABLE I

DETERMINATION OF MERCURY IN DILUTE MERCURIC CHLORIDE SOLUTIONS

No.	*Mercury present (mg)*	*Potassium iodide 0.01 N (ml)*	*Mercury found (mg)*	*Error (mg)*
1	5.0	4.92	4.93	−0.07
2	4.0	4.04	4.05	+0.05
3	3.0	3.04	3.05	+0.05
4	2.5	2.52	2.53	+0.03
5	2.0	2.04	2.05	+0.05
6	1.0	0.95	0.95	−0.05
7	0.64	0.60	0.60	−0.04
8	0.50	0.50	0.50	0.00
9	0.32	0.35	0.35	+0.03

Procedure for decomposing insoluble mercury compounds (inorganic or organic)

Method A. An amount of the substance containing 50–100 mg of mercury was weighed accurately into a dry 500-ml conical flask and 10 ml of aqua regia was added. The flask was covered with a glass and shaken well, and then placed on a hot plate (80°–90°) for about 10–15 min (30–40 min for organic compounds). The flask was then cooled and the solution was diluted to about 200 ml with distilled water. The solution was boiled for 3–4 min, cooled and filtered, if necessary, into a 500-ml measuring flask. The residue, if any, was washed free from chloride and the filtrate was diluted to the mark with distilled water. An aliquot containing 4–5 mg of Hg was taken for the titration.

Method B. In place of aqua regia, the sample could be digested with concentrated nitric acid followed by treatment with chlorine water.

Note. If the content of mercury is less than 50 mg, the digestion is carried out with 5 ml of aqua regia, or with concentrated nitric acid and chlorine water in a 150-ml conical flask, the volume is reduced by evaporation to remove excess acid (if the Hg content is less than 5 mg) and the final volume of the solution is diluted to 100 ml or 50 ml as necessary.

The results obtained for the determination of mercury in various inorganic con pounds are shown in Table II.

TABLE II

DETERMINATION OF MERCURY IN VARIOUS INORGANIC COMPOUNDS

Compound	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*
Mercuric oxide	5.0	4.92	—0.08
Mercurous chloride	5.0	4.95	—0.05
Mercuric sulphide	5.0	4.86	—0.14
Mercuric nitrate	5.0	5.06	+0.06
Mercuric sulphate	5.0	5.05	+0.05

Effect of bromide and iodide

For obvious reasons, the present titrimetric method could not be applied in presen of bromide and iodide. For the analysis of mercuric bromide or iodide, bromine ar iodine must be removed. Bromine can be removed by boiling the diluted solutic after digestion with aqua regia. The removal of iodine is not complete unless tl solution is evaporated just to dryness at 80°–90° or in vacuum. The results are shov in Table III.

TABLE III

DETERMINATION OF MERCURY IN MERCURIC BROMIDE OR IODIDE

Compound	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*	*Method of evaporation*
Mercuric bromide	5.0	4.66 (Average of 2 results)	—0.34	
	4.0	3.76 (Average of 2 results)	—0.24	
Mercuric iodide	5.0	4.81 (Average of 2 results)	—0.19	hot evaporation
	4.0	3.66 (Average of 2 results)	—0.34	hot evaporation
	2.0	1.86 (Average of 2 results)	—0.14	hot evaporation
	5.0	4.89	—0.11	vacuum desiccator
	4.0	3.88	—0.12	vacuum desiccator
	2.0	1.96	—0.04	vacuum desiccator

Determination of mercury in presence of impurities

Copper(II), iron(III) and zinc do not interfere, if sufficient periodate is preser The results in presence of iron are somewhat low; better results are obtained potassium fluoride is added before the addition of bicarbonate. The results are shov in Table IV.

Lead interferes with the titration but good results can be obtained by the followi procedure. To the neutral test solution containing mercury (2–5 mg) and lead (0.1

TABLE IV

DETERMINATION OF MERCURY IN PRESENCE OF COPPER(II), IRON(III) OR ZINC

No.	*Mercury present (mg)*	*Impurity (g)*	*Saturated KIO_4 solution (ml)*	*Other substances added (g)*	*Mercury found (mg)*	*Error (mg)*
1	5.0	0.05 of $CuSO_4 \cdot 5\ H_2O$	20	—	4.92	−0.08
2	5.0	0.10 of $CuSO_4 \cdot 5\ H_2O$	20	—	4.92	−0.08
3	4.0	0.05 of $CuSO_4 \cdot 5\ H_2O$	20	—	3.91	−0.09
4	4.0	0.10 of $CuSO_4 \cdot 5\ H_2O$	20	—	3.91	−0.09
5	4.0	0.05 of Fe(III)	25	—	3.61	−0.39
6	4.0	0.05 of Fe(III)	25	2.5 of KF	3.91	−0.09
7	5.0	0.05 of Fe(III)	25	2.5 of KF	4.91	−0.09
8	5.0	0.1 of Fe(III)	25	5.0 of KF	5.02	+0.02
9	4.0	0.05 of $ZnSO_4 \cdot 7\ H_2O$	20	—	3.91	−0.09
10	4.0	0.1 of $ZnSO_4 \cdot 7\ H_2O$	20	—	3.96	−0.04

0.3 g), potassium chloride (0.3 to 0.5 g) was added followed by potassium dihydrogen phosphate (0.3 to 0.5 g). The solution was then titrated as usual after addition of bicarbonate. The results are recorded in Table V.

TABLE V

DETERMINATION OF MERCURY IN PRESENCE OF LEAD

Lead compound $Pb(NO_3)_2$ (g)	*Potassium chloride (g)*	*KH_2PO_4 (g)*	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*
0.15	0.3	0.3	2.0	1.90	−0.10
0.25	0.3	0.3	2.0	1.95	−0.05
0.15	0.3	0.3	4.0	3.90	−0.10
0.25	0.3	0.3	4.0	3.90	−0.10
0.50	0.5	0.5	5.0	5.05	+0.05
0.50	0.5	0.5	5.0	5.15	+0.15

Moderate amounts of cations and anions such as Ca^{+2}, Mg^{+2}, Al^{+3}, SO_4^{-2}, AsO_4^{-3}, $H_2PO_4^-$ and NO_3^- do not interfere.

Organic mercury compounds have also been accurately analysed by this method. The results are compared with the calculated values of mercury obtained by other methods and are shown in Table VI.

TABLE VI

DETERMINATION OF MERCURY IN ORGANIC COMPOUNDS

Compound	*Mercury found (mg)*		*Mercury calc. (mg)*	*Mean error (mg)*	*Reagents used for decomposition*
Ethylmercuric chloride	3.56	3.56	3.70	0.14	aqua regia
	3.61	3.51	3.70	0.14	conc. HNO_3, Cl_2 water
Phenyl mercuric chloride	3.01	3.01	3.15	0.14	aqua regia
	3.01	3.06	3.15	0.11	conc. HNO_3, Cl_2 water
Mercurochrome	4.14	4.14	4.21	0.07	aqua regia[a]

[a] The residue obtained by evaporation of 2 ml of a 1% solution of mercurochrome to dryness can be decomposed easily by digestion with 2 ml of aqua regia.

Proprietary brands of mercury-containing pesticides

Owing to the difficulty of preparing small samples of pesticides accurately in the laboratory, two proprietary brands were analysed by this titrimetric method. The results are shown in Table VII.

TABLE VII

DETERMINATION OF MERCURY IN PESTICIDES

Material	*Mercury found (%)*	*Mercury found by other methods (%)*	*Reagents used for decomposition*
Ceresan (Bayer)	2.81 (Average of 2 results)	2.84	aqua regia
	2.87 (Average of 3 results)	—	conc. HNO_3
	3.01 (Average of 2 results)	—	conc. HNO_3, Cl_2 water
Agrosan GN (I.C.I.)	0.91 (Average of 2 results)	0.90	aqua regia[a]

[a] Satisfactory results were not obtained when this compound was decomposed with nitric acid

CONCLUSIONS

The proposed titrimetric procedure for the determination of small amounts of mercury can be applied to a wide range of preparations. The method is especially advantageous for the assay of 0.01 to 0.001% mercuric chloride solutions. The procedure is simpl and rapid, and the majority of preparations can be analysed in 15 to 30 min. Wit preparations containing organic substances, 40–45 min are required for analysis.

The results obtained in all the analyses, except those for mercuric bromide o iodide, are well within the limits of error permissible in semimicro or micro analysis

SUMMARY

Mercury(II) (0.5 to 5 mg) can be determined accurately by titration with potassium iodide solution in presence of potassium periodate and carbon tetrachloride as indicator. The simple an rapid method is applicable to many mercurial compounds and preparations; interferences are few

RÉSUMÉ

Une semi-micro méthode est proposée pour le dosage volumétrique du mercure(II), au moyen d'iodure de potassium. Ce procédé est simple et rapide.

ZUSAMMENFASSUNG

Beschreibung einer einfachen und raschen Halbmikro-Methode zur volumetrischen Bestimmung von Quecksilber(II) mit Kaliumjodid.

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HYDRAZINE AS A TITRIMETRIC REAGENT IN IODOMETRY

PART I

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Direct and indirect iodometric procedures are very widely used both in inorganic and organic analysis[1] but the traditional methods possess certain disadvantages. Standard iodine solution can be prepared by direct weighing[2] but this is somewhat inconvenient and therefore standardisation of an approximate solution is usually preferred. Arsenic trioxide is a well-established iodimetric primary standard but its use is generally limited to the standardisation of iodine solution and the preparation of standard arsenite solution is laborious. Sodium thiosulphate solution[3] is commonly used for the determination of free iodine; however, unless care is taken during its preparation, standardisation and storage, the reagent is not satisfactory. Moreover, there is a possibility of side-reactions owing to atmospheric oxidation and acid decomposition of the titrant. A general study of the disadvantages of thiosulphate, and to some extent sodium arsenite, has been made by BANKS[4].

A survey of methods showed that previous work has aimed either at determining hydrazine[5] itself or at its use as a direct reductant[6]. Because of the limitations of arsenite and thiosulphate solutions an attempt has been made to study the general behaviour of hydrazine as a reagent in iodometric titrations. This is not a new application[7] and no originality is claimed in this respect; however, we have studied the general use of the reagent in iodometry, as well as the optimum conditions for the iodometric determination of various substances. The direct and indirect determinations of a large number of substances are described below.

EXPERIMENTAL

Preparation, standardisation and stability of hydrazine solution

Free hydrazine base itself is unstable[8] but its hydrochloride and sulphate salts are quite stable. Analytically pure[5] salts can be easily prepared by recrystallisation of the C.P. product from water.

A 0.1 *N* solution of hydrazine was prepared by dissolving 2.6237 g of pure hydrazine hydrochloride (B.D.H.) in 1 l of glass-distilled water. The solution was stored in glass-stoppered bottles. Its concentration was checked by titrating against an iodine solution which had been standardised against sodium arsenite and bromate solution. The solution was highly acidic (pH 1.4 to 2) and was quite stable. The change in titre of the solution corresponded to only 0.05 ml of 0.1 *N* iodine solution when 100 ml were titrated after standing for a week.

General method for titrating excess or liberated iodine with hydrazine solution

The reaction between hydrazine and iodine is slow in acid medium[9] but rapid in presence of bicarbonate[10] (pH 7 to 7.4); excess of bicarbonate should be avoided because high results are obtained at high pH values owing to decomposition of hydrazine. A suitable amount of bicarbonate is 0.5–1 g per 25 ml of 0.1 *N* hydrazine solution. After iodine has been liberated from an aliquot of the test solution by adding potassium iodide in acid or neutral medium, the solution is neutralised with sodium bicarbonate. The titration is then carried out in presence of a slight excess of bicarbonate, the end-point being detected by the usual starch or starch glycollate indicator. Near the end-point the reaction is rather slow and the titrant must be added slowly with stirring. If the colour of the starch–iodide complex is obscured by the presence of other coloured substances, the end-point can be detected by the potentiometric "dead-stop" technique[11]. Sargent's Electrometric Titration Apparatus 'Ampot' with two similar platinum electrodes at an applied polarising potential of 20–30 mV was used in the present work. In presence of iodine the electrodes remain depolarised as indicated by a current of 15–20 mA flowing through the cell. In presence of excess of hydrazine the electrodes are polarised and the current reduces nearly to zero. Both the visual indicator method and the "dead-stop" technique gave identical and reproducible results but the latter method is to be preferred because of certain disadvantages of the starch indicator.

Permanganate, dichromate and cerium(IV)

In acidic medium dichromate, permanganate and cerium(IV) are reduced to definite lower valency states (Cr = 3, Mn = 2 and Ce = 3) by hydriodic acid, liberating equivalent amounts of iodine. After the free acid has been neutralised with bicarbonate the liberated iodine can be titrated with standard hydrazine solution as described above. Sufficient sample should be taken to consume 5–25 ml of 0.1 *N* hydrazine when the results are precise to ±0.3 to ±0.6%.

Copper sulphate

Iodine is liberated from solutions containing no free mineral acid by adding 1 g of potassium iodide per 0.6 g of copper sulphate present. The reaction mixture is then neutralised and titrated as above. The results are precise to ±0.5%.

Chlorate

To 10 ml of chlorate solution (*ca.* 0.2 *N*) are added 1 g of potassium bromide and 20 ml of concentrated hydrochloric acid (the final acid concentration should be 8 *N*). The flask is stoppered and allowed to stand for 5 min; 10 ml of 10% potassium iodide solution are then added and the titration is completed as before.

Bromate and iodate

Iodine is liberated from an aliquot of the test solution containing 0.5–2.5 mequiv. of bromate or iodate by adding 1 g of potassium iodide and sufficient hydrochloric acid, and the iodine is titrated as described earlier. In the case of bromate the reaction is slow and the reaction mixture should be allowed to stand for 2 min before the liberated iodine is titrated. The results are precise to ±0.3 to ±0.5%.

Periodate

To a solution of periodate containing 0.5 mmoles of the salt, 20 ml of saturated borax solution containing 0.5 g of boric acid are added followed by 2 g of potassium iodide; the liberated iodine is titrated as described above.

Hypochlorite and bleaching powder

2 g of potassium iodide and 10 ml of glacial acetic acid are added to the test solution and the liberated iodine is titrated as before.

Selenite

To 20 ml of approximately 0.05 N selenite solution are added 150 ml of water, 15 ml of starch solution, 10 ml of N potassium iodide and 10 ml of 5 N hydrochloric acid. The reaction mixture is allowed to stand for 15 min to complete the reduction of selenite to selenium and then titrated after neutralisation.

Hydrogen peroxide

To a 25-ml portion of *ca.* 0.1 N peroxide are added 10 ml of 4 N sulphuric acid and 6 ml of N potassium iodide followed by 3 drops of ammonium molybdate solution, and the liberated iodine is titrated as before. If ammonium molybdate is not added as catalyst, the reaction mixture should be allowed to stand for 15 min in a closed vessel before titration. The method can also be applied to metallic peroxides.

Ferricyanide and zinc

To 25 ml of a solution containing *ca.* 0.1 g of ferricyanide are added 20 ml of 10% potassium iodide, 2 ml of 2 N hydrochloric or sulphuric acid and 15 ml of a solution containing 2 g zinc sulphate. Liberated iodine is then titrated after neutralisation. Zinc sulphate[12] is added to prevent the back-reaction involving the conversion of ferrocyanide to ferricyanide.

By suitable modification, *i.e.* by employing an excess of ferricyanide and a definite amount of zinc solution, the method can also be employed for the determination of zinc.

Manganese dioxide

To a suspension of 150 mg of the powdered dioxide and 20 ml of 4 N phosphoric acid in a glass-stoppered flask is added sufficient bicarbonate to remove air followed by 1.5 g of potassium iodide. The flask is allowed to stand till all the dioxide has dissolved. The liberated iodine is then titrated as usual after neutralisation with sodium bicarbonate.

Sulphide, sulphite, phosphite and nitrite

Sulphide, sulphite, phosphite and nitrite are oxidised in acidic medium by standard iodine solution to sulphur, sulphate, phosphate and nitrate respectively but iodate–iodide mixture is preferable as a source of iodine. The solution containing 2.5 mmoles of the salt is mixed with the iodate–iodide mixture and then acidified. The excess iodine is then titrated as usual after standing for some time.

Mercurous mercury

To about 240 mg of mercurous chloride 25 ml of 0.1 *N* iodine and 1 g of potassium iodide are added and the mixture is shaken till the precipitate dissolves completely. It is then titrated as usual after neutralisation.

Ferrous iron

To the ferrous solution are added 5 ml of 4 *N* sulphuric acid and sufficient sodium bicarbonate to remove air from the flask; 5 g of powdered sodium pyrophosphate[13] are then added and the mixture is stirred till all the salt has dissolved. Iodine is then added and back-titrated after standing for a few seconds in the usual way.

Ferrocyanide

To about 25 ml of a solution containing 5–25 mmoles of ferrocyanide in an Erlenmeyer flask, are added 25 ml of 10% disodium monohydrogen phosphate solution, 25 ml of 20% acetic acid and 25 ml of 0.1 *N* iodine solution. The reaction mixture is then left in the dark for about 15–20 min and excess of iodine is titrated as usual.

Mercuric mercury

To 200 mg of mercuric chloride, 1–2 g of potassium iodide are added and shaken till the precipitate dissolves; 10 ml of 4 *N* sodium hydroxide solution and 3 ml of 35% formaldehyde are then added with continuous shaking, followed by 10 ml of water. After 2 min 10 ml of acetic acid and 25 ml of 0.1 *N* iodine solution are added. The reaction mixture is shaken till all the mercury dissolves and then excess of iodine is titrated after neutralisation.

DISCUSSION

The quantitative reaction of hydrazine and iodine is well established and in presence of a slight excess of sodium bicarbonate (pH = 7.4) the reaction proceeds rapidly and smoothly. The present study has shown that hydrazine can also be used for the titration of iodine liberated from iodide by certain oxidants such as permanganate, dichromate and cerium(IV), as well as for the determination of excess of iodine left after the oxidation of certain reductants.

It has been established that the reduction products of certain oxidants, *i.e.* Mn^{+2}, Cr^{+3}, Ce^{+3}, Zn^{+2}, Se, Cu_2I_2, Cl^-, Br^-, I^-, and oxidation products of certain reductants, *i.e.* Fe^{+3}, S, SO_4^{-2}, NO_3^-, PO_4^{-3} etc. do not interfere in the hydrazine–iodine reaction. Hydrazine can therefore be recommended as a suitable reagent in the iodometric determination of these compounds. Interference was observed in two cases, *i.e.* when ferric or ferrocyanide ions are present but this can be eliminated by complexing with phosphate or zinc ions respectively. Additional advantages of hydrazine salts are their availability in an analytically pure form which can be used as a primary standard, the stability of their solutions and the uniform conditions of the reaction with iodine. The disadvantage is that the cost of the reagent is higher than that of sodium thiosulphate. Iodometric determinations of other compounds, including organic substances, is under investigation and the results will be communicated shortly.

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SUMMARY

The preparation, standardisation and stability of hydrazine solution is described. The optimum conditions for the titration with hydrazine solution of pure iodine solution of iodine liberated from oxidants and of excess of iodine left after oxidation of certain reductants have been determined. The advantages of hydrazine over other iodometric reagents are discussed.

RÉSUMÉ

L'hydrazine peut être utilisée comme réactif pour le titrage iodométrique de nombreuses substances. Dans cette première partie, les auteurs ont examiné la préparation, l'étalonnage et la stabilité des solutions d'hydrazine.

ZUSAMMENFASSUNG

Beschreibung der Herstellung, Standardisierung und Stabilität von Hydrazinlösungen, deren Titration mit Jodlösung und Anwendung bei der Bestimmung von Oxydations- und Reduktionsmittel.

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REDOX INDICATORS IN INDIRECT TITRATIONS OF ANIONS

DETERMINATION OF PHOSPHATE IONS BY MEANS OF LEAD NITRATE

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INTRODUCTION

Titration of phosphates is normally accomplished by complexometric or alkalimetric methods. However, recently, it was proposed that anions could be titrated indirectly, by means of lead(II) nitrate in presence of redox indicators[1] the excess of lead being titrated with potassium ferrocyanide. Determinations of sulphate[2] and chromate[3] ions are also possible on this basis.

In the present paper, a similar indirect determination of phosphate ions is described. Excess of lead ions are titrated with potassium ferrocyanide solution in presence of variamine blue as a redox indicator. Previously, the same redox indicator[4] was used in the direct determination of phosphate ions with ferric nitrate, but this procedure does not give very accurate results and has many drawbacks.

EXPERIMENTAL

Reagent

1% Variamine blue solution (4-amino-4′-methoxydiphenylamine-acetate) in 20% acetic acid

Procedure

Two alternative methods are available:

(*a*) To the test solution of phosphate 2 ml of 1 *N* ammonium acetate, 2 ml of 1 *N* acetic acid and several ml of methyl alcohol were added. After this solution had been heated to boiling, excess of 0.1 *N* lead(II) nitrate was added dropwise with mechanical stirring. For high concentrations of phosphate ions 1 *N* lead nitrate solution was used. The solution was again boiled (to coagulate the precipitate) and then cooled, and the precipitate was filtered on a G4 crucible. It was then washed with an aqueous solution of methyl alcohol in such amounts that the final volume before titration was 100 ml and the methyl alcohol content amounted to 25%.

The filtrate was heated to about 60° and 3 drops of variamine blue solution and one drop of 0.1 *N* potassium ferricyanide were added. The sample was titrated with 0.1 *N* potassium ferrocyanide until the violet-blue colour changed to a permanent pale yellow; mechanical stirring was used.

(*b*) In the second method, the precipitate was not filtered. Otherwise the phosphate was determined as given in method (*a*), the same volume of solution (100 ml) and the same methyl alcohol content being used.

The same results were obtained in both cases.

Effect of foreign ions

Di- and trivalent cations interfere because they form insoluble phosphates and cannot be removed with alkali metal carbonates. Univalent cations interfere when their amount is greater than 5 times that of the excess of lead nitrate[2]. Anions which form precipitates with lead nitrate in presence of acetic acid also interfere.

DISCUSSION OF RESULTS

The influences of dilution and of the methyl alcohol content were tested. Under optimal conditions the reproducibility of results for the range 10–150 mg of phosphate is approximately 1.5%. The ferrocyanide solution must be standardized under identical conditions.

The results obtained by this titrimetric method agree with those of gravimetric determinations of phosphate as magnesium pyrophosphate (Table I).

TABLE I

GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF PHOSPHATE IONS

Sample	*Determination*		*Error*	
	Gravimetric mg	*Titrimetric*[a] *mg*	*mg*	%
1	178.5	175.0	—3.5	—1.96
2	176.3	174.0	—2.3	—1.30
3	176.1	174.0	—2.1	—1.19
4	176.0	174.0	—2.4	—1.10
5	175.1	174.0	—1.1	—0.63

[a] The volume of solution taken was only a fifth of that used for the gravimetric method.

SUMMARY

An indirect titration of phosphate with lead(II) nitrate solution is proposed; excess of lead is titrated with potassium ferrocyanide in presence of variamine blue as redox indicator.

RÉSUMÉ

Une méthode a été mise au point pour le dosage volumétrique indirect des phosphates par le plomb, dont on titre l'excès au moyen de ferrocyanure de potassium.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Phosphat mit einer Bleisalzlösung, deren Überschuss mit Kaliumferrocyanidlösung zurücktitriert wird.

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CHELATES OF 4-HYDROXYBENZOTHIAZOLE WITH THE RARE EARTHS

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The reactions of several types of chelating agents with the rare earths have bee investigated in recent years. Among the more important ligands that form chelate with the rare earths are dicarboxylic acids[1], amino acids[2], aminopolycarboxyli acids[3,4], β-diketones[5], cupferron[6], neocupferron[6], and 8-hydroxyquinoline and som of its derivatives[7]. Some workers have claimed that most of the rare earths form 1 : chelates with 8-hydroxyquinoline[7,8]. However it has subsequently been shown tha it is quite difficult to prepare rare earth oxinates having the expected 1 : 3 stoichi metry[9]. This is probably due to the contamination of these metal chelates with bas hydrolytic products of the rare earth cations.

Although 8-hydroxyquinoline and 4-hydroxybenzothiazole have similar chelat forming functionalities, the latter is more selective since it will not react with titaniu vanadium, molybdenum and tungsten[10]. The investigation of the chelating tendenci of 4-hydroxybenzothiazole towards the rare earths is an extension of the previou work carried out in this laboratory in order to evaluate the factors that give rise t the selectivity of 4-hydroxybenzothiazole[11].

EXPERIMENTAL

Preparation of metal solutions

Stock solutions of the lanthanides were prepared by dissolving weighed amounts metals or their oxides in nitric acid and diluting to an appropriate volume with wate Table I gives the purity of the materials used. The solutions were not standardize

TABLE I

PURITY OF METALS AND METAL OXIDES USED

Metal or metal oxide	*% Purity*
Y_2O_3, Pr_6O_{11}, Nd_2O_3, Tb_4O_7, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3	99.9
La, Gd	99.6
Ce	98
Sm	99·97
Eu_2O_3	99.8
Dy	99·5
Ho	99·3

Hydrolysis of metal nitrates in 50% v/v ethanol–water

A measured volume of the metal nitrate solution was made up to contain 50% v/v of ethanol and titrated with 0.1 *M* carbonate-free sodium hydroxide at 25 ± 0.2°. The solution was first degassed with nitrogen and an atmosphere of nitrogen was maintained in the titration vessel throughout the titration. After the excess acid in the metal nitrate solution was neutralized, the standard sodium hydroxide was added in small increments (0.1–0.2 ml). A volume of ethanol equal to the volume of the standard base was added after each increment, in order to maintain the ethanol–water ratio at 50% v/v. The pH of the solution was measured not less than 10 min after each addition of standard base in order to ensure that equilibrium was reached. All pH measurements were made with a Beckman Model G pH meter equipped with a glass–saturated calomel electrode pair and calibrated with buffer solutions at pH 4.00 and 7.00. From the titration curves obtained, the pH values at which the metal ions hydrolyzed could be determined.

Preparation of metal chelates

The preparation of 4-hydroxybenzothiazole has been published[11]. A 0.1-*M* solution of 4-hydroxybenzothiazole in ethanol was added to the metal nitrate solution. The resulting solution contained about 50% v/v of ethanol and a 4 : 1 ratio of 4-hydroxybenzothiazole: metal ion. The pH of the solution was raised slowly and with stirring by the dropwise addition of 1 : 1 ammonia. The pH at which the first permanent precipitate was obtained was noted and 2 to 3 drops more of ammonia solution was added. In all cases the pH at which the metal chelate precipitated was below the pH at which hydrolysis of the metal ion occurred. The resulting solution was warmed on a water-bath until the precipitate coagulated. The solution was filtered and the precipitate washed with water and ethanol. The chelates were dried in a vacuum desiccator to constant weight and analyzed.

Titrimetric determination of 4-hydroxybenzothiazole

A weighed amount of 4-hydroxybenzothiazole was dissolved in 2 *N* hydrochloric acid and a measured excess of standard potassium bromate–bromide solution added, the excess being determined iodometrically with starch as the indicator. The precision and accuracy obtained in this bromometric titration of 4-hydroxybenzothiazole was unsatisfactory, especially for the titration of small quantities of 4-hydroxybenzothiazole. All determinations were subsequently carried out using an amperometric indicator circuit for the detection of the end-point[12].

A stock solution containing 0.15 mg of 4-hydroxybenzothiazole per ml was made in 1 *N* hydrochloric acid. An aliquot of this solution was added to the titration vessel together with 1 g potassium bromide. The total volume was made up to about 40 ml, sufficient hydrochloric acid being present in the solution to make the solution about 1 *N* in hydrochloric acid. The titrant was 0.002 *M* potassium bromate in 0.1 *M* potassium bromide. A rotating platinum microelectrode, rotated with a Sargent synchronous motor, was used as the indicator electrode. This indicator electrode and a standard calomel electrode were placed in the titration vessel, and short-circuited through a microammeter. The potential of the saturated calomel electrode was sufficiently negative for the current in the indicator system to be proportional to the amount of free bromine in solution. A plot of current *vs.* volume of titrant gave an L-shaped titration curve from which the end-point was readily located. No correction for blank titration was applied, since this was negligibly small. In all titrations a correction was made for the volume change that occurred during the titration.

Titrimetric determination of 4-hydroxybenzothiazole chelates

A weighed amount of the chelate was dissolved in 12 *N* hydrochloric acid and diluted to an appropriate volume in a volumetric flask with distilled water. Aliquots of this solution were used for the bromometric titration as described for 4-hydroxybenzothiazole. All solutions titrated were about 1 *N* in hydrochloric acid. The results obtained are given in Table II, each result being the average of 2–4 determinations

TABLE II

TITRIMETRIC DETERMINATION OF THE RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZOLE

Metal	*% Ligand found*	*% Ligand calculated for 1 : 3 chelate*
La	76.10	76.42
Pr	73.63	76.17
Nd	75.20	75.74
Sm	72.53	74.97
Eu	74.10	74.76
Gd	71.26	74.12
Tb	73.82	73.91
Dy	67.61	73.48

Gravimetric determination of 4-hydroxybenzothiazole chelates

The rare earth chelates of 4-hydroxybenzothiazole were ignited in a Pregl micro muffle furnace and weighed as the oxides. The results of several determinations are averaged and given in Table III.

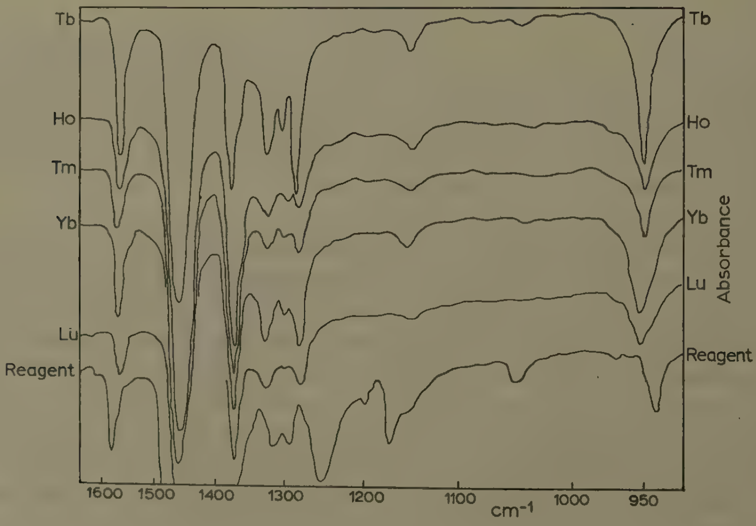

Fig. 1a.

nfrared spectra of 4-hydroxybenzothiazole chelates

All spectra were recorded with a Perkin Elmer Model 21 double-beam spectro-hotometer equipped with sodium chloride optics, employing Nujol mulls of the netal chelates. The infrared spectra obtained are shown in Fig. 1 and summarized n Table IV.

RESULTS

ince the solubility of 4-hydroxybenzothiazole in water was low, a solution of the ompound in ethanol was used for precipitating the chelates from aqueous solutions

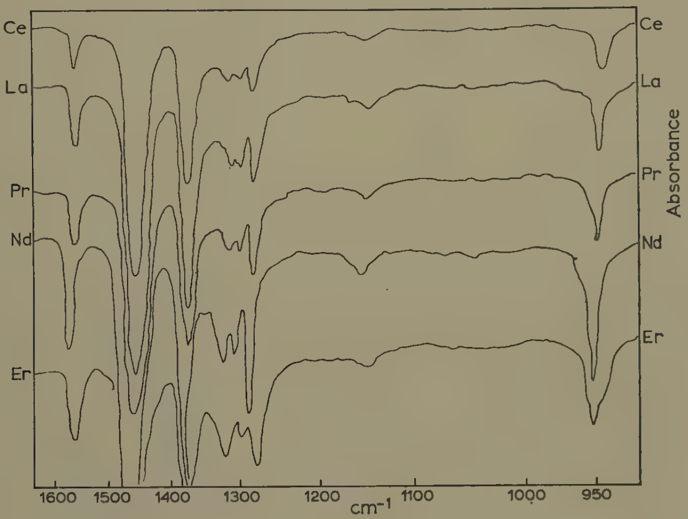

Fig. 1b.

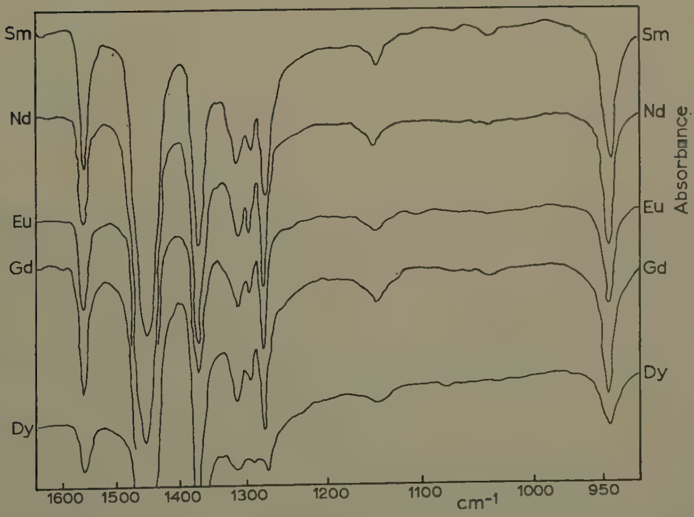

Fig. 1c

Fig. 1. Infrared spectra of the rare earth chelates of 4-hydroxybenzothiazole.

TABLE III

MICROGRAVIMETRIC DETERMINATION OF THE RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZO

Metal	*% Metal found*	*% Metal calculated for 1:3 chelate*
Ce	24.46	23.73
Pr	20.99	23.83
Nd	24.43	24.26
Sm	23.73	25.03
Eu	24.95	25.24
Gd	24.82	25.88
Tb	21.46	26.09
Dy	24.16	26.52
Ho	26.76	26.81
Er	26.92	27.08
Tm	27.37	27.28
Yb	29.94	27.76
Lu	27.79	27.98

TABLE IV

INFRARED SPECTRA OF RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZOLE

Metal chelate	*Strong* cm^{-1}	*Medium* cm^{-1}	*Weak* cm^{-1}
La	1553, 944, 765, 1276	1310, 1148, 1294	717
Ce	1555, 1278, 946	1312, 1148	1296, 718
Pr	1558, 946, 1278	1310, 766, 1296	718
Nd	1560, 1280, 947, 767	1312	1298, 1150, 827, 805, 719
Sm	1560, 1278, 945, 764	1313, 1147	1294, 826, 805
Eu	1560, 1280, 947, 766	1317, 1150	1298, 807, 746, 717
Gd	1563, 1280, 948, 766	1317, 1150	1297, 806, 738, 719
Tb	1560, 947, 1277, 765	1318, 1150	1298, 881, 827, 809, 738, 717
Dy	1562, 1277, 947	1316, 765	1294, 736, 717
Ho	1560, 1278, 947	1318, 1146, 763	1293, 883, 733, 718
Er	1563, 1277, 950, 765	1320, 1150	1295, 883, 805, 732
Tm	1563, 1278, 948	1320, 1148, 764	1293, 885, 734, 718
Yb	1565, 950, 1276	1323, 1150, 765	1295, 805, 732
Lu	1565, 1278, 952	1320, 1148, 763	1295, 733, 718

of the rare earth nitrates. In all cases the maximum concentration of ethanol in th solution was 50% v/v. In order to prevent coprecipitation of any hydrolysis produc of the rare earths during the precipitation of the metal chelates, the pH of the ethano water solutions was not allowed to exceed the pH at which hydrolysis occurred. Th latter pH values were determined from the titration curves for the hydrolysis of th rare earth nitrates in 50% ethanol–water solutions. The pH values reported by MOE LER AND KREMERS[13], at which the hydrolysis of rare earth nitrates in aqueous sol tions occurred, were confirmed. Also the pH at which hydrolysis occurred decrease as the atomic number of the metal increased. Therefore all rare earth chelate precip tations were carried out below a pH of 6.0. In most cases a permanent precipitate the rare earth chelate with 4-hydroxybenzothiazole was formed at a pH between 4 and 5.5.

It was found necessary to devise a method for the determination of 4-hydroxybenzothiazole in its chelates. A bromometric titration based on the formation of the 5,7-dibromo compound[14] was found to be unreliable if starch solution was used as he indicator. However using an amperometric indicator system it was found that a .5 · 10^{-4} M solution of 4-hydroxybenzothiazole could be titrated with an error of less than 1%. This method was employed for the determination of 4-hydroxybenzothiazole n some of its rare earth chelates. The results are summarized in Table II.

DISCUSSION

From the analytical results shown in Table II it is probable that most of the rare earth chelates of 4-hydroxybenzothiazole have a 1 : 3 metal : ligand ratio although there are several cases in which the data are difficult to interpret. Both titrimetric and gravimetric methods give low results for the chelates of Pr, Dy, Gd and Sm. It is possible that in these cases a definite number of moles of water are associated with the chelates. Any attempts to remove this water by drying at elevated temperatures resulted in the decomposition of the chelates. If it is assumed that three moles of water are associated with the Dy chelate and two moles of water with the Gd and Sm chelates, the calculated values in Tables II and III agree reasonably well with experimental values. On the other hand it is quite possible that in the case of Pr, a non-stoichiometric complex was formed since Pr_6O_{11} was the source of the praseodymium ion which may have existed in solution in more than one oxidation state. The low result obtained gravimetrically for the percentage of Tb in its chelate was probably due to a mixture of oxides formed when the chelate was ignited in the micromuffle furnace. The titrimetric method using an amperometric indicator circuit gave poor results for the chelates of Ce, Ho, Er, Tm and Yb. It was found that errors of about 10% were obtained and n addition there was considerable difficulty in locating the end-point in the titration n the presence of these rare earths.

It has become apparent from this work that 4-hydroxybenzothiazole is not a particularly suitable reagent for either the separation or determination of the rare earths. Most of the rare earth chelates are precipitated in approximately the same pH range and it is evident that it is quite difficult to prepare stoichiometric complexes and also to avoid coprecipitation of hydrolysis products of the rare earths. In spite of the fact that the pH at which these chelates were precipitated was below the pH at which hydrolysis occurred, it is nevertheless possible that some contamination with hydrolytic products of the metal ions may have been obtained.

The infrared spectra of the chelates of the elements in the first transition series with 4-hydroxybenzothiazole were examined and empirical assignments made for the C–O vibrations in the chelates[11]. It was therefore of interest to determine whether these assigned frequencies could be located in the infrared spectra of the rare earth chelates. On the basis of the shifts of the C–O vibration frequencies in the transition metal chelates, it was found possible to make certain qualitative predictions concerning the stability of these chelates[11]. A similar attempt was made to correlate the chelate stability with shifts in the C–O vibration frequencies in the rare earth metal chelates of 4-hydroxybenzothiazole. Fig. 1 and Table IV give the results obtained.

The infrared spectra of the rare earth chelates are very similar to one another, as is to be expected, if all the compounds contain a 1 : 3 metal : ligand ratio. The strong band between 1555 cm^{-1} and 1565 cm^{-1} as well as the band of medium intensity between

1310 cm^{-1} and 1320 cm^{-1} can be attributed to C–O vibrations in these chelates[1] The positions of these bands are shifted by only 10 to 15 cm^{-1} in going from the lar thanum to the lutecium chelate. This is an extremely small shift corresponding to a energy difference of 30–45 cal and any correlations that can be made would b fortuitous. However it can be seen that there is a general tendency for this band t shift to higher wave numbers with increasing atomic weight or atomic number. Thi is suggestive of the fact that there may be little change in the stability constants the chelates of the metals in this series, and the changes if any would tend to make th rare earths of higher atomic number form more stable chelates than those of low atomic number.

ACKNOWLEDGEMENT

The authors are grateful to the U.S. Atomic Energy Commission for financial assis ance.

SUMMARY

The rare earth chelates of 4-hydroxybenzothiazole have been prepared and analyzed by a titr metric method as well as a microgravimetric method. The infrared spectra of these chelates ha been determined.

RÉSUMÉ

Les auteurs ont effectué une étude sur les chélates de l'hydroxy-4-benzothiazole obtenus av les terres rares.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Chelate der seltenen Erden mit 4-Hydroxybenzothiaz

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MICRODOSAGE COLORIMÉTRIQUE DU BORE EN MILIEU AQUEUX, AU MOYEN DE RÉACTIFS À GROUPEMENT AZOÏQUE OU IMINE DÉRIVÉS DES ACIDES H ET K

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Paris (France)

(Reçu le 4 octobre 1960)

Les réactions servant au dosage colorimétrique de petites quantités d'acide borique, très sensibles et spécifiques, ont généralement toutes le défaut de ne pouvoir être développées en milieu aqueux, et la pollution par l'humidité des milieux réactionnels peut, en certains cas, fausser gravement les dosages.

On s'est proposé d'étudier les réactions colorées permettant le micro-dosage colorimétrique du bore en milieu aqueux; elles sont peu nombreuses et ne semblent guère avoir été utilisées jusqu'ici: à citer celle à l'acide chromotropique mentionnée par KUEMMEL ET MELLON[1], encore que la sensibilité de cette réaction semble être assez moyenne.

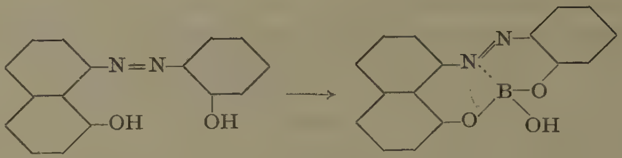
Le présent travail a pour origine les réactions colorées indiquées par KORENMAN[2], KORENMAN ET SHOGANOVA[3], POLUEKTOV ET NIKONOVA[4]. Ces auteurs envisagent, il est vrai, quelques réactions colorées, au reste classiques, que donne l'acide borique, en milieu aqueux et alcalin, avec l'aluminon ou avec des dérivés hydroxy-anthraquinoniques (alizarine, quinalizarine, etc.); la sensibilité de tels réactifs est faible, la dilution limite est seulement 1 pour 10,000, et atteint rarement 1 pour 100,000. Il n'en sera pas traité dans ce qui suit: les réactifs opérant en milieu aqueux et acide présentent, en effet, un intérêt beaucoup plus net.

Sont rappelées ci-après les règles établies expérimentalement par POLUEKTOV ET NIKONOVA[4], s'agissant de la structure des réactifs qui donnent des colorations en milieu aqueux acide. Ceux-ci résultent de la combinaison des acides amino-α naphtol-disulfoniques avec un phénol par l'intermédiaire d'une fonction azoïque ou d'une fonction imine.

Ne réagissent pas avec l'acide borique, les oxyazoïques contenant un seul hydroxyle ou encore plusieurs hydroxyles sur le même noyau, par exemple: le dérivé obtenu à partir de la *m*-nitroaniline diazotée avec le phénol.

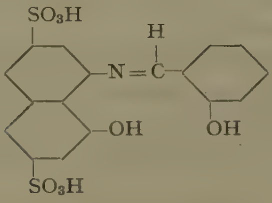
Ne réagissent pas non plus avec l'acide borique, les azoïques où deux hydroxyles sont dans deux noyaux différents, en *ortho* par rapport au groupement azoïque, par exemple: le dérivé obtenu à partir de l'acide amino-1-naphtol-2-sulfonique-4 et de la résorcine.

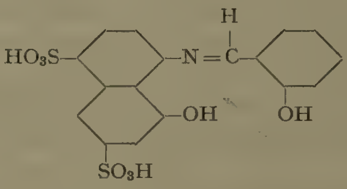
Par contre, donnent une réaction colorée avec l'acide borique les azoïques comportant dans un noyau naphtalénique un OH en péri par rapport au groupement azoïque, et sur l'autre noyau (naphtalénique ou phénylé) un OH en *ortho*. La réaction consiste en un virage, qui a lieu par chauffage en milieu acétique à 80–100°, puis refroidissement. Il s'agit vraisemblablement d'une chèlation par le bore, portant les oxydriles, par exemple:



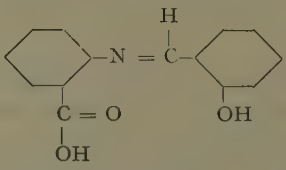
Dans les réactions colorées obtenues avec les réactifs du type azoïque l'on peut, selon KORENMAN[2,3], POLUEKTOV ET NIKONOVA[4], remplacer le groupement azoïque par le groupement imine, il s'agit alors des réactifs du type azométhine. Les mêmes règles, quant à la place des fonctions phénoliques et des fonctions azotées valent dans l'un et l'autre cas.

On obtient de tels composés en condensant par exemple les acides H ou K avec l'aldéhyde salicylique:





Le réactif de KORENMAN s'obtient en mélangeant 1 volume de solution alcoolique à 5% d'aldéhyde salicylique avec 13 volumes d'une solution aqueuse d'acide H ou d'acide K à 1%. À 2.5 ml d'une solution aqueuse contenant de l'acide borique, ajouter 2 ml d'acide acétique *N* et 0.5 ml du réactif précédent: une coloration jaune intense apparaît, alors que le témoin obtenu dans des conditions identiques, mais sans addition d'acide borique, reste coloré en jaune pâle. A remarquer que la base de Schiff obtenue par condensation de l'acide anthranilique avec l'aldéhyde salicylique donne également une réaction colorée jaune avec le bore, mais la sensibilité en ce cas est faible et la dilution limite est de 1/10,000 seulement (KORENMAN[2,3]).



KOULBERG ET BADEVEVA[5] ont synthétisé et isolé le réactif de KORENMAN et abouti aux composés purs résultant de la combinaison des acides H ou K avec l'aldéhyde salicylique*. Le mécanisme de la réaction colorée des azométhines est selon ces auteurs différent de celui de la réaction que donnent les réactifs à groupement azoïque.

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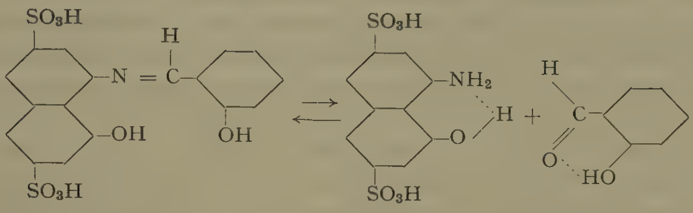
* Que l'on appellera pour simplifier Azométhine H ou K.

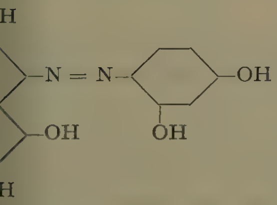
Alors que l'acide borique provoque un virage de la coloration des réactifs azoïques, en revanche il ne fait qu'accentuer la coloration initiale des azométhines.

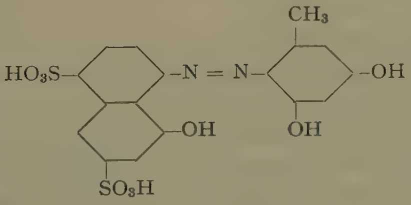
Ainsi en solution aqueuse l'azométhine H par exemple se dissocierait selon le schéma:



Or, en solution aqueuse, seule l'azométhine H est colorée en jaune, alors que l'acide H et l'aldéhyde salicylique sont pratiquement incolores. En l'absence d'acide borique ces deux produits ne se combineraient l'un à l'autre que très lentement par suite de la position des groupements fonctionnels en *ortho*, et de la nécessité de la rupture des liaisons hydrogène de l'acide H et de l'aldéhyde salicylique. En présence d'acide borique, celui-ci formant facilement des esters avec les fonctions phénoliques, les groupements — NH_2 et — CHO se trouvent libérés et pourraient ainsi se combiner entre eux plus aisément. En définitive, l'acide borique agirait comme un catalyseur qui permettrait à l'équilibre ci-dessus décrit, de se déplacer de droite à gauche, et par suite de condenser l'azométhine, seule substance colorée.

En résumé, les réactifs en question sont des colorants résultant de la combinaison des acides amino-naphtoldisulfoniques avec des polyphénols par l'intermédiaire d'une fonction diazotée, ou avec des aldéhydes comportant un groupement phénolique par l'intermédiaire d'une fonction iminée. Plus particulièrement, ont été retenus par les auteurs soviétiques[4,6] les acides H et K combinés avec les substances que mentionne le Tableau I ci-après; la réaction est un virage du jaune ou du jaune orangé au rouge ou rouge violet pour les colorants azoïques, et une accentuation de la coloration du jaune au jaune plus foncé pour les colorants azométhines. Exemples:





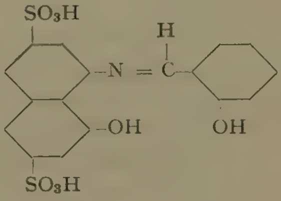


TABLEAU I

Azoïques		*Azométhines*
Acide H et résorcine	Acide K et résorcine	Acide H et aldéhyde salicylique
Acide H et orcine	Acide K et orcine	Acide K et aldéhyde salicylique
Acide H et phloroglucine		
Acide H et pyrogallol		
Acide H et β-naphtol		

MICRODOSAGE DU BORE À L'AIDE DES RÉACTIFS DU TYPE AZOMÉTHINE

L'étude des réactifs de ce groupe résulte de la technique semi-quantitative de Korenman[2,3].

À 2.5 ml de la solution neutre de bore à étudier, ajouter 2 ml d'acide acétique *N* et 0.5 ml d'un réactif formé d'un volume de solution alcoolique à 5% d'aldéhyde salicylique et de 13 volumes d'une solution aqueuse à 1% d'acide amino-8-naphtol-1-disulfonique-3,6 (acide H) ou d'acide amino-8-naphtol-1-disulfonique-3,5 (acide K). L'acide borique provoque une coloration jaune intense, l'essai témoin exempt de bore étant coloré en jaune pâle.

La même réaction est obtenue en remplaçant le mélange d'acide H (ou K) et d'aldéhyde salicylique par le produit cristallisé résultant de leur combinaison (azométhine H ou azométhine K) selon Koulberg et Badeveva[5].

On s'est attaché partant de là, à étudier ces réactions dans le domaine quantitatif. À titre d'indication, des quatre étudiés, le réactif à l'azométhine H présente l'intérêt le plus grand.

Matériel utilisé

Il est fait usage de matériel en silice. Les mesures photométriques sont faites au moyen du spectrophotomètre Jean et Constant.

Réactif à l'azométhine H

*Synthèse de l'azométhine H**

Dissoudre 18 g d'acide H dans un litre d'eau distillée. Tiédir pour faciliter la dissolution. Filtrer. Neutraliser en versant goutte à goutte une solution d'hydroxyde de potassium à 20% jusqu'à virage au Rouge Congo (essai à la touche). Puis réacidifier légèrement en versant goutte à goutte de l'acide chlorhydrique au demi jusqu'à acidification au Rouge Congo (essai à la touche avec virage au bleu très franc). Ajouter un excès de 15 ml d'acide environ (pour avoir un pH de 1.5–3.0). Placer la solution sous un agitateur mécanique et verser goutte à goutte 20 g d'aldéhyde salicylique fraîchement distillé. Agiter énergiquement pendant une heure. Laisser déposer le fin précipité orangé d'azométhine H pendant une nuit. Filtrer sur entonnoir de Büchner. Laver plusieurs fois à l'alcool éthylique, puis à l'éther. Sécher à l'étuve (90–105°) jusqu'à poids constant.

L'azométhine H est une poudre légère d'un orangé clair; elle se décompose à 300° en dégageant de l'aldéhyde salicylique. Elle est soluble dans l'eau, assez peu soluble dans l'alcool méthylique ou éthylique, et insoluble dans l'éther, le benzène, le toluène, le chloroforme, l'acétone, le tétrachlorure de carbone.

Le produit étant légèrement hygroscopique doit être conservé sitôt après étuvage en flacon soigneusement bouché placé lui-même si possible dans une cage à dessiccation.

Mode opératoire

Réactifs

Acide sulfurique ($d = 1.83$) dilué au cinquième (1 : 4) avec de l'eau distillée; Solution d'acétate d'ammonium à 500 g/l; Acide acétique cristallisable et Ammoniaque pure ($d = 0.925$).

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* Cette technique indiquée par Koulberg et Badeveva[5] a été revue par nous sur certains points de détail. La synthèse de l'azométhine K s'effectue selon une technique en tout point identique en remplaçant l'acide H par de l'acide K.

Réactif à l'azométhine H

Azométhine H[*], 6 g; Acide ascorbique, 20 g; Eau distillée q.s.p., 1 l.

Liqueur titrée d'acide borique à 10 μg de bore par ml

Peser 5.7135 g d'acide borique cristallisé, séché au dessiccateur à acide sulfurique. Dissoudre le produit dans de l'eau distillée et compléter à 1 l en fiole jaugée avec de l'eau distillée. Diluer au centième la solution précédente avec de l'eau distillée en s'aidant d'une fiole jaugée.

1 ml de cette dernière solution contient 10 μg de bore.

Eau distillée

Peut être obtenue au moyen d'un alambic en cuivre étamé, mais l'emploi d'un appareil distillatoire en silice est cependant plus recommandable. L'eau épurée par passage de l'eau ordinaire sur résines anionique et cationique est à proscrire formellement.

Courbe d'étalonnage

Dans une série de béchers[**] de 100 ml, introduire successivement : 0, 1, 2, 3 . . . 7–8 ml de liqueur titrée d'acide borique contenant 10 μg de bore par ml, 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au cinquième[***] et 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 5.20 (contrôle à l'électrode de verre) au moyen d'acide acétique ou d'ammoniaque au demi. Transvaser en fioles jaugées de 100 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 10 ml[+] de réactif à l'azométhine H. Compléter à 100 ml avec de l'eau distillée. Agiter et laisser la coloration se développer à l'obscurité, à 20° ± 5°, pendant 18 h.

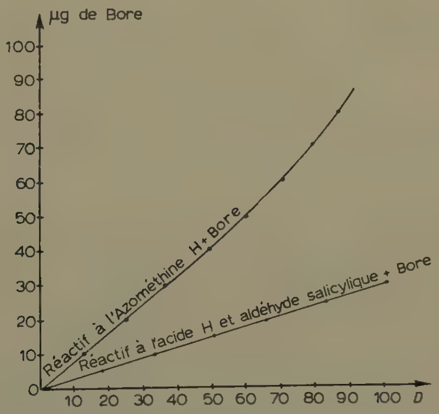

Fig. 1. Courbes d'étalonnage obtenues avec le réactif à l'azométhine H et avec le réactif à l'acide H et aldéhyde salicylique.

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[*] L'azométhine H doit être pesé très exactement.

[**] Pour toutes les opérations effectuées à froid du matériel en pyrex peut être utilisé. L'emploi de matériel en silice reste cependant plus recommandable.

[***] L'addition d'acide sulfurique au cinquième n'est pas indispensable.

[+] À mesurer très exactement.

Au bout de ce temps, les colorations des différents termes de la gamme d'étalonnage sont mesurées par rapport à celle du terme zéro, à $\lambda = 415$ mμ.

Les résultats obtenus sont ceux représentés dans la Fig. 1*. La courbe obtenue est pratiquement une droite entre 0 et 50 μg de bore.

Dosage

La solution neutre contenant l'acide borique à doser (entre 0 et 100 μg de bore) est traitée selon la technique de la gamme d'étalonnage.

Discussion

Étude qualitative du réactif

Le réactif a été préparé selon les deux formules suivantes: *Réactif A*: azométhine H, 0.6 g et eau distillée q.s.p., 100 ml; *Réactif B*: azométhine H, 0.6 g, acide ascorbique, 2 g et eau distillée q.s.p., 100 ml.

Dans des fioles jaugées de 100 ml sont distribués successivement: 30 ml de solution titrée d'acide borique (1 ml = 1 μg de bore), 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au cinquième, 10 ml de solution d'acétate d'ammonium à 500 g/l, 10 ml de Réactif A ou B et eau distillée q.s.p. 100 ml. Des témoins correspondants sans bore ont été préparés.

Un essai et un témoin de chacune des séries A et B a été placé pendant 24 h à l'obscurité, l'autre essai ou témoin de chaque série restant exposé pendant le même temps à la lumière du jour. Des observations faites à des intervalles de temps réguliers montrent que dans tous les essais avec bore une coloration jaune se développe assez lentement pour atteindre son complet développement au bout de 6 h environ, tandis que les témoins sans bore restent pratiquement incolores. Au bout de 24 h les essais et témoins A (sans acide ascorbique) laissés à la lumière du jour présentent un très léger brunissement par rapport aux mêmes essais ou témoins laissés à l'obscurité; par contre dans les essais ou témoins B (avec acide ascorbique) aucun brunissement n'apparaît.

Ces résultats montrent que le réactif à l'azométhine H préparé en présence d'acide ascorbique (réactif B) est plus stable à l'air et que les colorations doivent de préférence être développées à l'obscurité.

Influence de la longueur d'onde sur l'absorption de la lumière incidente

Deux essais contenant 30 μg de bore ont été préparés avec du réactif B en suivant la même technique. Avant de compléter les volumes à 100 ml, les pH des deux essais ont été réglés à pH 5.0 et 6.15 avec de l'acide acétique ou de l'ammoniaque. Deux témoins correspondants sans bore ont également été préparés. Après 18 h de développement à l'obscurité les colorations ont été mesurées par rapport à de l'eau distillée.

La Fig. 2 représente les résultats obtenus. Le maximum d'absorption se situe donc vers $\lambda = 415$ mμ à pH 5.0.

Influence du pH sur l'intensité de la coloration

Une série d'essais contenant 30 μg de bore et des témoins correspondants exempts de bore sont amenés à différents pH par introduction d'acide acétique ou d'ammoniaque (contrôle à l'électrode de verre). Après 18 h de développement à l'obscurité, les colorations des différents essais ont été mesurées par rapport à leurs témoins correspondants, à $\lambda = 415$ mμ.

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* Avec cuves de 2 cm; la sensibilité du spectrophotomètre étant réglée pour correspondre à une tare optique de 60.

Selon les résultats obtenus qui sont représentés sur la Fig. 3, l'intensité de la coloration est maximale vers pH 5.2, et elle reste pratiquement constante entre pH 4.8 et 5.6.

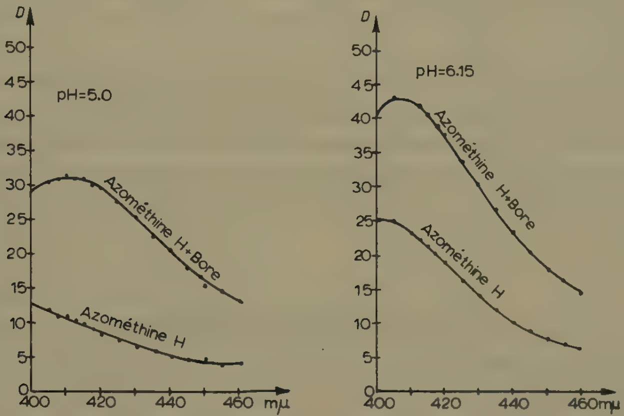

Fig. 2. Courbes d'absorption du réactif à l'azométhine H et du complexe coloré azométhine H + bore en fonction de la longueur d'onde, à pH 5.0 et 6.15

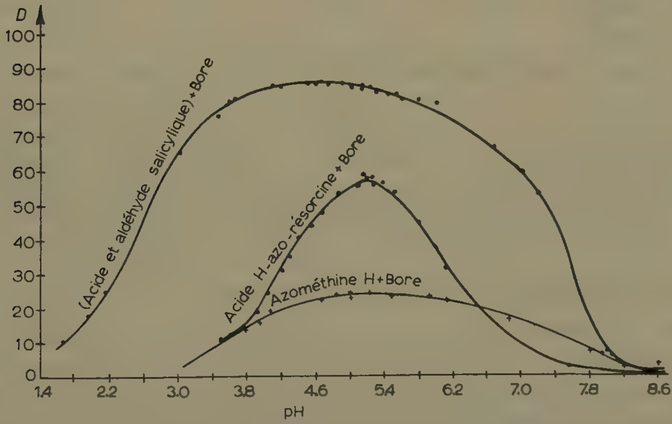

Fig. 3. Influence du pH sur l'intensité de la coloration du complexe coloré azométhine H + bore; du complexe coloré obtenu avec le réactif à l'acide H et aldéhyde salicylique + bore; et du complexe coloré obtenu avec le réactif à l'acide H –azo–résorcine + bore.

À remarquer que la coloration jaune pâle des témoins augmente progressivement quant le pH s'élève. Dans la zône de pH 8.0–9.0 la coloration jaune des témoins est presque aussi intense que celle des essais.

Vitesse de développement de la coloration

Une série d'essais contenant 30 μg de bore et de témoins sans bore a été préparée selon la technique précédente, le pH final étant de 5.2. Les essais et témoins sont placés à l'obscurité, la température étant de 20° ± 5°, et des mesures de coloration des différents essais par rapport à leurs témoins sont faites à des intervalles de temps qui ont été notés.

Les résultats obtenus représentés sur la Fig. 4 montrent que le développement de la coloration due au bore est rapide pendant les cinq premières heures, puis se ralentit considérablement pour tendre vers une limite qui n'est atteinte qu'après plusieurs jours de contact.

Les mesures photométriques doivent donc être effectuées après un temps déterminé qui doit rester le même dans tous les cas. L'on peut en fait effectuer les mesures après 18 h de repos, la vitesse de développement de la coloration devenant alors suffisamment faible pour permettre d'obtenir des résultats constants et reproductibles.

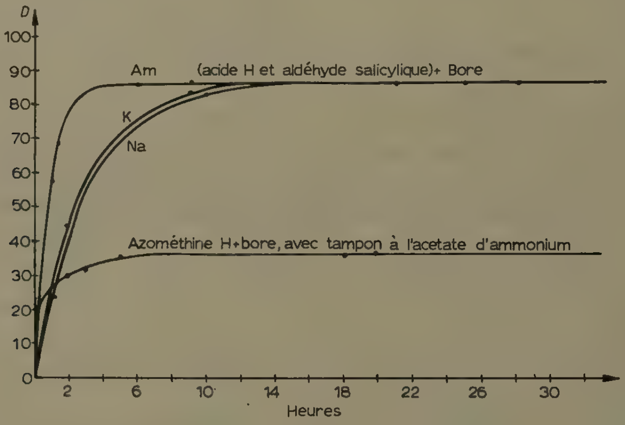

Fig. 4. Vitesse de développement de la coloration du complexe coloré azométhine H + bore, à 20° ± 5°, en présence d'acétate d'ammonium utilisé comme tampon. Vitesse de développement de la coloration du complexe coloré obtenu avec le réactif à l'acide H et aldéhyde salicylique + bore en présence de tampon sodique, potassique et ammonique.

Influence de la température sur l'intensité de la coloration

L'expérience a montré qu'entre 5° et 25° l'intensité de la coloration obtenue en présence d'une quantité fixe de bore reste pratiquement constante. Par chauffage (vers 50°) la coloration obtenue en présence de bore augmente considérablement, mais celle des témoins exempts de bore varie de la même façon. De plus, un brunissement de fond se superpose alors à la coloration jaune normale, de sorte que la différence de coloration entre l'essai et le témoin est finalement plus faible. En définitive, les colorations peuvent être commodément développées à 20° ± 5°.

Influence de la concentration du réactif en azométhine H

L'intensité de la coloration obtenue dépend étroitement de la quantité d'azométhine H présente dans le milieu réactionnel, ainsi que le montrent les résultats du

Tableau II, obtenus en présence d'une quantité constante de bore, soit 30 μg, et d'un même volume de réactif dont la concentration en azométhine H était variable. Dans tous les cas le pH est égal à 5.2.

TABLEAU II

Essai No.	*Concentration du réactif en azométhine H (g/l)*	*Déviations photométriques*	*pH essai*	*pH témoin*
1	3	15	5.23	5.23
2	4	23	5.25	5.25
3	5	29	5.25	5.25
4	6	35	5.25	5.25
5	7	39.5	5.25	5.25

On a donc intérêt à utiliser un réactif aussi concentré que possible en azométhine H. Mais l'expérience ayant montré qu'il est assez difficile de dissoudre à froid 7 g d'azométhine H par litre, c'est donc la composition du réactif indiquée dans mode opératoire qui a été adoptée.

Ordre d'introduction des réactifs

Cet ordre a une influence assez marquée sur la reproductibilité des résultats. En effet, une certaine dispersion dans les résultats a été observée lors d'essais dans lesquels le réactif avait d'abord été introduit, puis où le pH avait été ajusté par tâtonnement avec de l'acide acétique ou de l'ammoniaque au demi. La quantité d'ammoniaque ajoutée ayant été trop forte en certains cas et la valeur visée du pH dépassée, il a fallu réacidifier partiellement par l'acide acétique. Dans de telles conditions l'addition d'ammoniaque augmente visiblement l'intensité de la coloration jaune des témoins, laquelle n'est sans doute que partiellement diminuée quand l'on réacidifie par de l'acide acétique.

Les résultats sont au contraire très réguliers et reproductibles quand le réactif à l'azométhine H est ajouté en dernier après fixation du pH.

Influence des éléments étrangers

Les éléments suivants: Sb, As, Ba, Bi, Cd, Ca, Cs, Co, K, Li, Mg, Mn, Nd, Ni, Nb, Pb, Re, Se, Na, Sr, Ta, Te, Tl, Th, W, U et Zn, ainsi que NO_3^-, $P_2O_5^{-3}$, Cl^-, F^-, SO_3^{-2}, $C_2O_4^{-2}$ et WO_3, ne donnent aucune coloration avec le réactif.

Na^+ et K^+ ralentissent le développement de la coloration. Sn(II), Te et Hg(II)

TABLEAU III

Elément gênant	*Poids de l'élément gênant qui donne avec le réactif à l'azométhine H la même coloration que 1 µg de bore*
Mo (MoO_3)	625
Zr	25
Al	2.1
Be	0.5
Ti	11.1
V(IV)	2.5
V(V)	2.5
Cu	4.5
Cr	11.1

donnent un précipité blanc. Cu et Cr donnent une coloration jaune brun. Fe(II), Fe(III), ainsi que l'ion nitrite NO_2^- donnent un fort brunissement. Les sulfites empêchent la coloration de se développer. Les molybdates donnent une coloration jaune très faible s'ils sont en quantité trop importante. Enfin Al, Be, Ti, Zr, V(IV), V(V) et Ga donnent une coloration jaune très intense.

Dans le Tableau III on a reproduit le poids des différents éléments gênants qui donne avec le réactif à l'azométhine H la même coloration que 1 µg de bore.

Résumé

Les paramètres expérimentaux de la réaction de l'azométhine H avec le bore, en milieu aqueux acide, ont été précisés: introduction d'acide ascorbique comme anti-oxygène, domaine de pH, longueur d'onde optimale, influence de la température; le complet développement n'est atteint qu'après plusieurs jours de contact et les mesures seront faites après écoulement d'un temps déterminé convenablement.

Du point de vue pratique, l'acétate d'ammonium étant employé comme tampon les mesures photométriques peuvent être effectuées après repos de 18 h à l'obscurité la température ambiante restant comprise entre 15° et 25°. Le pH optimum de 5.2 peut en fait varier entre pH 4.8 et 5.6. Longueur d'onde optimale pour les mesures $\lambda = 415$ mµ.

L'intensité de la coloration dépend des quantités présentes de bore et d'azométhine H, ce qui oblige pour les mesures à employer des quantités exactement mesurées d'un réactif dont la composition optimale a été déterminée.

La sensibilité du nouveau réactif a été trouvée voisine de 0.01 µg de bore par ml c'est-à-dire équivalente à celles d'autres réactifs plus classiques.

Quelques éléments, dont la liste a été indiquée, peuvent gêner et doivent être soigneusement éliminés s'ils sont présents.

Réactif à l'azométhine K

L'étude de ce réactif a montré que l'azométhine K obtenu en remplaçant l'acide H par de l'acide K, a des propriétés absolument analogues à celles de l'azométhine H.

Tout ce qui a été dit précédemment est donc entièrement valable lorsqu'il est fait usage de l'azométhine K; toutefois la longueur d'onde optimale pour les mesures (absorption maximale) a été trouvée à $\lambda = 417.5$ *mµ* au lieu de 415 mµ.

Réactif à l'acide H et aldéhyde salicylique

Le réactif indiqué par KORENMAN[2,3] et dont la composition a été indiquée antérieurement, n'est en fait pas stable à l'air, il se produit un brunissement assez rapide surtout à la lumière du jour. Pour empêcher ce brunissement il est nécessaire d'ajouter un réducteur. Là encore l'acide ascorbique s'est montré le réducteur le mieux approprié.

Réactifs particuliers

Solution A (à préparer extemporanément): acide amino-8-naphtol-1-disulfonique-3,6 (acide H), 1 g; acide ascorbique, 2 g; eau distillée q.s.p., 100 ml.

Solution B: aldéhyde salicylique (fraîchement distillé), 5 g; alcool éthylique à 95° q.s.p., 100 ml.

Le réactif s'obtient en mélangeant au moment de l'emploi 13 volumes de solution A et 1 volume de solution B, soit 91 ml de solution A et 7 ml de solution B.

Par ailleurs, les mêmes réactifs que ceux déjà indiqués antérieurement.

Courbe d'étalonnage

Dans une série de béchers de 50 ml, introduire successivement: 0, 1, 2, 3. . . . 7–8 ml de liqueur titrée d'acide borique contenant 10 μg de bore par ml et 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 4.60 avec de l'acide acétique (ou de l'ammoniaque) au demi (contrôle à l'électrode de verre). Transvaser en fioles jaugées de 50 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 5 ml de réactif à l'acide H et aldéhyde salicylique. Compléter à 50 ml avec de l'eau distillée. Agiter et laisser la coloration se développer à l'obscurité, à 20° ± 5°, pendant 18 h.

Au bout de ce temps, les colorations des différents termes de la gamme d'étalonnage sont mesurées par rapport à celle du terme zéro, à $\lambda = 415$ mμ. La courbe d'étalonnage obtenue est celle représentée dans la Fig. 1*.

Dosage

La solution neutre contenant l'acide borique à doser (entre 0 et 50 μg de bore) est traitée selon la technique de la gamme d'étalonnage.

Discussion

Étude qualitative du réactif: Le réactif à l'acide H + aldéhyde salicylique donne également, en solution aqueuse acide, une coloration jaune intense avec le bore, mais les témoins correspondants sans bore sont nettement plus colorés en jaune que ceux obtenus avec le réactif à l'azométhine H étudié ci-dessus. Malgré l'addition d'acide ascorbique la stabilité à l'air du réactif est un peu moins bonne que celle du réactif à l'azométhine H, un très léger brunissement de fond peut se produire si les essais avec ou sans bore restent exposés trop longtemps à une lumière trop vive. Il faut donc effectuer les mesures assez rapidement (en moins d'une heure) dès que les essais sont sortis de l'obscurité.

La longueur d'onde optimale pour les mesures: se situe, comme dans le cas du réactif à l'azométhine H, à $\lambda = 415$ mμ.

Influence du pH sur l'intensité de la coloration due au bore: Celle-ci a été déterminée en distribuant dans une série de béchers de 50 ml: 2.5 ml de solution titrée de bore, dont 1 ml contient 10 μg de bore, 10 ml de solution d'acétate d'ammonium à 500 g/l et une quantité variable d'acide acétique ou d'ammoniaque pour amener le pH de chacun des termes à une valeur comprise entre pH 1.4 et 8.6.

Après transvasement en fioles jaugées et rinçage des béchers avec quelques ml d'eau distillée, addition de 5 ml de réactif à l'acide H + aldéhyde salicylique. Après quoi, le volume de chaque terme est complété à 50 ml avec de l'eau distillée. Agitation. Par ailleurs des témoins correspondants exempts de bore ont été établis parallèlement. Après 18 h de développement à l'obscurité (température ambiante: 20° ± 5°), la coloration des différents essais a été mesurée par rapport à celle des témoins correspondants à λ = 415 mμ. Les résultats obtenus sont reproduits dans la Fig. 3.

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* En cuves de 2 cm également, et avec le même réglage de la sensibilité du spectrophotomètre que précédemment.

La déviation photométrique maximale est donc obtenue vers pH 4.60; toutefois entre pH 4.10 et 5.15, les résultats peuvent être considérés comme constants.

Vitesse de développement de la coloration: La cinétique de la réaction colorée est la même que dans le cas du réactif à l'azométhine H. L'acétate d'ammonium étant utilisé comme tampon, la coloration peut être mesurée pratiquement après repos de 18 h; mais s'il est fait usage de l'acétate de sodium ou de potassium, la coloration est plus longue à se développer, comme le montrent les résultats représentés sur la Fig. 4.

Influence de la température sur l'intensité de la coloration: Entre 0 et 25°, les colorations obtenues en présence d'une quantité fixe de bore peuvent être considérées comme constantes. Pratiquement des résultats très reproductibles sont obtenus en développant les colorations à 20° ± 5°.

Influence de la composition du réactif sur l'intensité de la coloration: La quantité de bore en expérience restant constante et le volume ajouté de réactif restant également constant, l'intensité de la coloration obtenue dépend étroitement de la concentration du réactif en acide H et en aldéhyde salicylique; par contre la quantité ajoutée d'acide ascorbique n'a guère d'influence. Il est donc nécessaire de préparer très exactement le réactif et de le conserver identique dans une même série de dosages.

Après 18 h de développement à l'obscurité les résultats obtenus sont alors très reproductibles. Les mesures photométriques doivent être faites assez rapidement, car après une heure d'exposition à la lumière du jour, une baisse déjà sensible de la coloration peut être observée.

Les colorations obtenues avec le réactif à l'acide H et aldéhyde salicylique sont donc moins stables que celles obtenues avec le réactif à l'azométhine H.

Ordre d'introduction des réactifs: Les meilleurs résultats ont encore été obtenus en n'introduisant qu'après établissement du pH approprié le réactif à l'acide H et aldéhyde salicylique.

Influence des éléments étrangers: Mêmes observations que pour le réactif à l'azométhine H.

Conclusion

Le réactif à l'acide H et aldéhyde salicylique a donc des propriétés sensiblement analogues à celles du réactif à l'azométhine H. Il en diffère toutefois sur les points suivants: pH optimal pour les mesures trouvé égal à 4.60, avec résultats pratiquement constants entre pH 4.10 et 5.15, coloration jaune plus intense des témoins et moins bonne stabilité des colorations que de celles obtenues avec l'azométhine H.

Réactif à l'acide K et aldéhyde salicylique

L'étude de ce réactif, obtenu en remplaçant dans le réactif précédent l'acide H par de l'acide K, a montré que les deux réactifs ont des propriétés identiques, à l'exception de la longueur d'onde optimale qui a été trouvée de 417.5 mμ au lieu de 415 mμ.

Autres colorants dérivés de l'acide H

Quelques essais ont également été effectués en remplaçant l'acide H par des colorants dérivés de l'acide H. Les principaux colorants utilisés ont été les suivants:

Noir naphtalène 12 BN (C.I.: 20.470 Acid black 1). Vert noir pour laine J (C.I.: 20.495 Acid Green 20), Bleu diazol 2 B (C.I.: 22.610 — Direct blue 6), Bleu diazol V (C.I.: 23.710 — Direct blue 21), Noir diazol BH (C.I.: 22.590 — Direct blue 2), Bleu pur diazol 4 B (C.I.: 24.400 — Direct blue 15) et Vert para 2 BL(Bayer) (C.I.: 22.230).

En aucun cas il n'est apparu la moindre trace de coloration en présence de bore, même après repos de plusieurs jours. Ceci montre que la réactivité à l'égard du bore des composés ayant la structure de base énoncée par POLUEKTOV ET NIKONOVA[4] cesse de se manifester si la structure moléculaire devient trop compliquée, ou si les diverses positions du noyau naphtalène sont trop encombrées.

En résumé, de tous les réactifs à groupement imine étudiés précédemment seul a été retenu l'azométhine H.

MICRODOSAGE DU BORE EN MILIEU AQUEUX ACIDE À L'AIDE DE RÉACTIFS À GROUPEMENT AZOÏQUE

Parmi les nombreux réactifs indiqués par POLUEKTOV ET NIKONOVA[4] les deux suivants obtenus par diazotation de l'acide H ou de l'acide K avec la résorcine ont été seulement étudiés*.

Réactif à l'acide (azo-1'-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,6 (acide H-azo-résorcine)

Réactif à l'acide H-azo-résorcine

Colorant, 0.100 g** et eau distillée q.s.p., 1 l. Par ailleurs, les mêmes réactifs que ceux déjà indiqués pour l'étude du réactif à l'azométhine H.

Courbe d'étalonnage

Dans une série de béchers de 100 ml distribuer successivement: 0, 1, 2, 3 . . . 7 ml de solution titrée d'acide borique dont 1 ml contient 10 μg de bore. Puis dans chaque bécher ajouter: 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au cinquième*** et 10 ml de solution d'acétate d'ammonium à 500 g/l.

Régler le pH à 5.20 par de l'ammoniaque ou de l'acide acétique (contrôle à l'électrode de verre). Transvaser dans une série de fioles jaugées de 100 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 10 ml de réactif à l'acide H-azo-résorcine+. Compléter à 100 ml avec de l'eau distillée. Agiter. Après repos de 72 h à l'obscurité, (la température restant comprise entre 16° et 20°), la coloration des différents termes de la gamme est mesurée par rapport à celle du terme zéro exempt de bore.

Les résultats obtenus sont représentés dans la Fig. 5++. La courbe ne suit donc pas la loi de LAMBERT-BEER, et il y aurait intérêt dans ces conditions à effectuer les mesures en colorimétrie différentielle.

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* Ces deux colorants, ainsi que ceux dérivés de l'acide H dont il a été fait mention, nous ont été fournis gracieusement par la Société Francolor, à qui vont nos remerciements.

** Le colorant doit être pesé très exactement.

*** L'addition d'acide sulfurique dilué au cinquième n'est pas indispensable.

+ Le réactif doit être mesuré très exactement.

++ En cuves de 2 cm, et avec même réglage de la sensibilité du spectrophotomètre que précédemment.

Dosage

La solution neutre contenant l'acide borique à doser (0 à 50 μg de bore) est traité selon la technique de la gamme d'étalonnage.

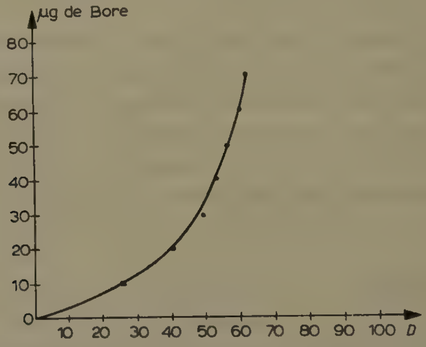

Fig. 5. Courbe d'étalonnage obtenue avec le réactif à l'acide H-azo-résorcine.

Discussion

Étude qualitative et choix du réactif: Au moyen des deux réactifs suivants: *Réactif* Colorant, 0.100 g et eau distillée q.s.p., 1 l; *Réactif B:* Colorant, 0.100 g, acide asco bique, 20 g et eau distillée q.s.p., 1 l les essais suivants ont été effectués.

Dans des fioles jaugées de 100 ml verser: 5 ml de solution titrée d'acide boriqu dont 1 ml contient 10 μg de bore, 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au ci quième, 10 ml de solution d'acétate d'ammonium à 500 g/l et 10 ml de réactif A ou Compléter à 100 ml avec de l'eau distillée. Agiter. Préparer des témoins correspo dants exempts de bore.

Certains des essais et des témoins de chaque série sont laissés à l'obscurité et l autres sont maintenus à la lumière du jour.

Il est observé que tous les essais avec bore, d'abord colorés en jaune orangé vire peu à peu au rouge orangé, et le complet développement de la coloration n'est attei qu'après plusieurs heures (65 h environ); elle reste ensuite stable pendant plusieu jours. Les témoins exempts de bore restent colorés en jaune orangé.

Dans tous les essais avec bore et dans les témoins sans bore laissés à la lumière jour, il apparaît peu à peu un très léger brunissement.

La coloration rouge des essais avec bore ayant reçu une addition d'acide ascorbiq (réactif B) se développe progressivement pour atteindre son maximum d'intensité bout de 45 h environ, mais diminue ensuite progressivement, et après 5 ou 6 jou les essais et témoins préparés avec le réactif B sont très nettement décolorés. L'ad tion d'acide ascorbique n'est donc pas bénéfique.

Il ressort de ces essais que les meilleurs résultats sont obtenus en utilisant le réac A, et en laissant les colorations se développer à l'obscurité. Ce réactif a été ado définitivement.

Absorption de la lumière incidente en fonction de la longueur d'onde par le coloran le complexe coloré (colorant + bore). Un essai et un témoin exempt de bore s maintenus pendant 65 h à l'obscurité; puis la coloration de l'essai et celle du tém sont mesurées par rapport à de l'eau distillée, à différentes longueurs d'onde. I résultats obtenus sont représentés sur la Fig. 6. Le complexe coloré (en présence de bore) présente un maximum d'absorption à $\lambda = 515$ mμ environ, et pour le colorant seul le maximum se situe à $\lambda = 480$ mμ environ. Si l'on mesure la variation de densité optique du complexe coloré avec bore par rapport à celle du colorant seul, le maximum d'absorption, donc la sensibilité maximale pour les mesures, se situe à $\lambda = 515$ mμ.

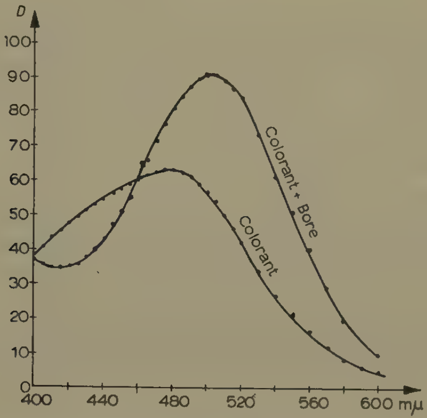

Fig. 6. Courbe d'absorption du colorant (acide H-azo-résorcine) et du complexe coloré avec le bore (colorant + bore).

Influence du pH sur l'intensité de la coloration due au bore: Dans des essais contenant une quantité constante de bore (soit 50 μg), on a fait varier progressivement le pH d'un terme à l'autre par addition de quantités variables d'acide acétique ou d'ammoniaque. Des témoins de même pH exempts de bore sont préparés parallèlement.

Après repos de 65 h à l'obscurité la densité optique des essais est mesurée par rapport à celle des témoins sans bore correspondants. Les résultats obtenus, représentés sur la Fig. 3, montrent que l'intensité de la coloration obtenue avec le bore est très sensible à l'influence du pH, et que le maximum d'intensité est obtenu à pH 5.20 environ (pratiquement les résultats restent constants entre pH 5.15 et 5.25).

Influence de la température et de la durée sur le développement de la coloration due au bore: Le développement de la réaction colorée de l'acide borique avec le réactif étudié est accéléré par chauffage et l'intensité de la coloration obtenue est fonction de la température à laquelle elle a été développée. Le Tableau IV résume les observations relevées.

À la température de 16–20°, la coloration se développe lentement pour atteindre on maximum d'intensité après 65 h; il faut 85 h à la température de 12 à 15°. L'intensité de la coloration reste alors stable pendant plusieurs heures, ou même plusieurs jours.

À chaud, la coloration se développe beaucoup plus vite, mais elle n'est ni stable, ni onstante en intensité. Ainsi, dès 40°, les témoins se décolorent progressivement, ainsi que les essais contenant du bore. Les résultats ne sont ni constants, ni réguliers. l est donc nécessaire que la réaction soit faite à froid, et à température constante, t que les mesures soient effectuées au bout d'un temps déterminé, qui doit rester e même dans tous les cas.

Le plus aisé est de laisser la coloration se développer à une température de 16–20°, et d'effectuer en ce cas les mesures photométriques après 72 h de repos à l'obscurité, l'intensité maximale de la coloration étant alors pratiquement atteinte.

TABLEAU IV

Essai	Température de développement de la coloration	pH	*Déviations photométriques obtenues après développement de la coloration pendant:*											
			2 h	*5 h*	*8 h*	*18 h*	*24 h*	*26 h*	*42 h*	*51 h*	*65 h*	*72 h*	*88 h*	*150 h*
A	12–15°	5.20				25		37	46	51	56.5	57	58.5	58.5
B	16–20°	5.20				30.5		41.5	49.5	53.5	56	56	56	56
C	40–42°	5.20		32	40	48	41	37.5	28	25.5	23.5			
D	64–65°	5.20		35	28									
E	95–100°	5.20	26	25										

Influence de la concentration du réactif en colorant sur l'intensité de la coloration obtenue avec le bore: Dans le mode opératoire déjà indiqué antérieurement, on a remplacé les 10 ml de réactif contenant 0.100 g de colorant par litre, par 10 ml de réactif contenant 0.200 g ou 0.300 g de colorant par litre. Les résultats indiqués dans le Tableau V montrent que l'intensité de la coloration dépend étroitement de la quantité de colorant introduite.

TABLEAU V

Essai	*Quantité présente de bore dans les essais*	*Concentration du réactif en colorant (g/l)*	*Déviations photométriques*	*pH essai*	*pH témoin*
1	50 μg	0.100	28	5.20	5.20
2	50 μg	0.200	53.5	5.20	5.20
3	50 μg	0.300	74	5.20	5.20

Du point de vue pratique, l'expérience montrant que les témoins No. 2 et 3, préparés avec du réactif contenant 0.200 g ou 0.300 g de colorant par litre, sont très fortement colorés en jaune, il a été jugé préférable de retenir seulement le réactif déjà utilisé et contenant 0.100 g de colorant par litre.

Influence des éléments étrangers: Les éléments Sb, As, Ba, Bi, Cd, Ca, Ce, Cs, Di, Li, Mg, Mn, Nd, Ni, Nb, Pb, K, Re, Se, Na, Sr, Ta, Te, Tl, W, Zn, ainsi que NO_3^-, $P_2O_5^{-3}$, Cl^-, F^-, SO_3^{-2}, $C_2O_4^{-2}$, WO_3 ne donnent pas de coloration avec le réactif.

Na et K ralentissent le développement de la coloration. Co, Fe, Mo, U, Hg, Au

TABLEAU VI

Elément gênant	*Poids de l'élément gênant qui donne avec le réactif la même coloration que 1 μg de bore (μg)*
Cr	5,000
Cu	1,660
Al	1,250
Be	715
Ti	1,660
V(IV)	455
V(V)	625

Pt, SO_2 et NO_2, entraînent un brunissement plus ou moins intense du réactif. Sn, Te et Hg(II) donnent un précipité blanc. Be, Cr, Cu, Al, Th, Ti, V et Zr donnent une coloration rouge plus ou moins intense. La correspondance en bore de chacun de ces éléments gênants est indiquée dans le Tableau VI.

Résumé

Le colorant azoïque constitué par l'acide H et la résorcine (acide (azo-1′-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,6) donne avec le bore, en milieu aqueux acide, une coloration rouge qui ne se développe que très lentement. À la température ambiante (16–20°), le complet développement n'est obtenu qu'au bout de 65 h, la coloration reste alors stable pendant plusieurs jours.

L'intensité de la coloration obtenue est très sensible à l'influence de la température, du pH et de la concentration du réactif en colorant. Par chauffage, la vitesse de développement peut être augmentée, mais les résultats obtenus ne sont ni réguliers, ni stables.

Les mesures doivent être effectuées dans des conditions toujours identiques quant à la durée et à la température de développement de la coloration, au pH, et à la concentration du réactif.

Les conditions optimales sont les suivantes quand on utilise de l'acétate d'ammonium comme tampon: Développement à l'obscurité, à la température de 16–20°, pendant 72 h; pH optimal: 5.20, les résultats étant pratiquement identiques pour des valeurs du pH comprises entre 5.15 et 5.25; longueur d'onde optimale pour les mesures: 515 mμ; la courbe d'étalonnage n'est pas une droite; sensibilité: 0.01 μg de bore par ml environ; de nombreux ions gênent et doivent être éliminés s'ils sont présents.

Réactif à l'azoïque de l'acide K et de la résorcine (acide (azo-1′-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,5)

La structure de ce composé a déjà été indiquée dans le Tableau I. L'étude de ce réactif a montré qu'il présente des propriétés pratiquement analogues à celles du précédent sous réserve des quelques points de détail suivants: Longueur d'onde optimale pour les mesures (sensibilité maximale) observée à 520 mμ; influence encore plus marquée du pH sur l'intensité de la coloration (pH optimal; 5.20 avec résultats pratiquement identiques entre pH 5.15 et 5.25 seulement); développement beaucoup plus lent de la coloration, dont le complet développement n'a été obtenu qu'après repos de 325 h à la température de 16–20°; sensibilité analogue à l'égard du bore (soit 0.01 μg de bore par ml environ); mêmes interférences des éléments étrangers.

Autres colorants

Les autres colorants suivants, bien que n'ayant pas la structure fondamentale énoncée par Poluektov et Nikonova[4] ont néanmoins été expérimentés:

acide amino-2-phénolsulfonique-4 acide amino-2-phénolsulfonique-4	Acide N,N′-bis[hydroxy-1-(hydroxy-2′-sulfo-5′-phénylazo)-2-sulfo-3-naphtyl-6]urée.

amino-2-phénol-sulfonamido-4 amino-2-phénol-sulfamide-4	Acide N,N′-bis[hydroxy-1-(hydroxy-2′-sulfo-5′-phénylazo)-2-sulfo-3-naphtyl-6]urée.
chloro-4-amino-2-phénol chloro-4-amino-2-phénol	Acide N,N′-bis[hydroxy-1-(hydroxy-2-′sulfo-5′-phénylazo)-2-sulfo-3-naphtyl-6]urée.
acide amino-2-phénolsulfonique-4	Acide dihydroxy-1,8-naphtalène disulfonique-3,6.
acide amino-1-naphtol-2-sulfonique-1,4	Acide naphtol-1-sulfonique-8.

Bordeaux au chrome solide R (C.I. 14.290 Mordant Red 5).

En aucun cas, aucune coloration n'est apparue en présence de bore, ce qui confirme bien l'hypothèse de POLUEKTOV ET NIKONOVA[4] concernant la structure que doivent avoir les colorants pour donner une réaction colorée avec le bore en milieu aqueux acide.

RÉSUMÉ

Différents réactifs préparés avec des colorants comportant des groupements imine ou azoïque ont été expérimentés en vue du microdosage colorimétrique du bore en milieu aqueux acide. Au total, 19 réactifs ou colorants différents ont ainsi été essayés, dont 6 seulement se sont montrés utilisables, et les conditions d'emploi de ces 6 réactifs ont été étudiées et précisées. Les résultats obtenus montrent que, de tous ces réactifs, le plus pratique et le plus commode d'emploi est de loin celui à l'azométhine H (dérivé de l'acide H et de l'aldéhyde salicylique). La sensibilité de ce réactif à l'égard du bore est équivalente à celle d'autres réactifs classiques, mais il offre sur ceux-ci l'avantage important d'opérer en milieu aqueux. Le réactif n'est cependant pas entièrement spécifique du bore; un certain nombre d'éléments peuvent gêner et doivent être éliminés s'ils sont présents. Le réactif à l'azoïque de l'acide H et de la résorcine présente également un certain intérêt; il est cependant beaucoup moins avantageux que le précédent.

SUMMARY

For the colorimetric microdetermination of boron, 19 dye-stuffs containing imine or azo groups have been examined; only 6 of these were usable and much the best was azomethine-H. This reagent can be used in aqueous media.

ZUSAMMENFASSUNG

Für die colorimetrische Mikrobestimmung von Bor wurden 19 verschiedene Farbstoffe, die Imin- oder Azogruppen enthalten geprüft, von denen sich 6 als brauchbar erwiesen. Keiner ist jedoch dem Azomethin H überlegen.

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DIE BESTIMMUNG VON LITHIUM IN SILIKATISCHEN MINERALIEN (ZINNWALDITKONZENTRAT) MITTELS FLAMMENPHOTOMETRIE

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Bei der direkten flammenphotometrischen Bestimmung von Lithium in Zinnwalditkonzentraten treten Störungen infolge anwesender Begleitelemente wie Si, Fe, Mn, Mg, Al, Na und K auf, deren Kompensation mittels Rahmenlösungen für alle auftretenden Kombinationen zu umfangreich wird. Es erfolgt deshalb eine Abtrennung der Schwer- und Erdalkalimetalle durch einen Anionen-Ionenaustauscher in der Oxalat- und EDTA-Form und eine Auftrennung der Alkalien mittels eines Kationenaustauschers. Im Vergleich dazu wird eine vorherige Abtrennung der Störelemente mit Cadmiumoxyd und basischem Bleicarbonat durchgeführt.

Apparatives

Zur Lithium- und Kalium-Bestimmung diente ein Flammenphotometer No. III der Fa. Zeiss Jena mit einem vorgeschalteten Metallinterferenzfilter Li 67 (671 ± 7 nm) für Lithium und K 76 (768 ± 8 nm) für Kalium. Die Störelementabtrennung erfolgte einmal in einer Kationenaustauschersäule (Durchmesser 10 mm, Höhe 1120 mm, Austauscher: Wofatit KPS 200 der Fa. VEB Farbenfabrik Wolfen, Körnung 0.2–0.3 mm, beladen mit Wasserstoffionen, Austauschkapazität 33.6 mg K/cm und 28.6 mg Na/cm Harz), zum anderen Male in einer Anionenaustauschersäule (Durchmesser 120 mm, Höhe 550 mm, Austauscher: Wofatit L 150 der Fa. VEB Farbenfabrik Wolfen, Körnung 0.3–0.4 mm; zur Hälfte war die Säule mit EDTA und mit Oxalat beladen).

Aufschluss

Ca. 1 g Zinnwalditkonzentrat wurde mit einem Gemisch aus 5 ml conz. Salpetersäure und 10 ml Fluorwasserstoffsäure (40%-ig) dreimal aufgeschlossen und die zurückbleibende Substanz dreimal mit conz. Schwefelsäure abgeraucht. Anschliessend wurde mit 25 ml 50%-iger Schwefelsäure solange gekocht, bis die Lösung klar erschien (vgl. ELLESTAD UND HORSTMANN[1]).

TRENN- UND BESTIMMUNGSMETHODEN

(*a*) Zur direkten Flammenphotometrie wurde die aufgeschlossene Substanz auf 250 ml aufgefüllt und davon 25 ml zur Analyse verwendet. Es wurde gegen Rahmenlösungen, die die entsprechenden Mengen Natrium und Kalium enthielten, mit einem Li-Filter gemessen.

(*b*) Zur Auftrennung der Alkalien wurde eine Kationenaustauschersäule mit KPS 200 nach Jentzsch und Frotscher[2] eingesetzt. Es zeigte sich, dass infolge der anderen anwesenden Elemente wie Eisen, Aluminium, Mangan usw. die Säulen in Kürze blockiert wurden, sodass eine Abtrennung dieser Elemente vorher erfolgen musste.

(*c*) Die Abtrennung der Störelemente Eisen, Mangan, Aluminium, usw. wurde mit einem Anionenaustauscher Wofatit L 150 durchgeführt. Die Anordnung wurde bereits unter Apparatives geschildert (vgl. dazu Samuelson *et al.*[3–5]). Das Filtrat dieser Trennung wurde dann zwei bis dreimal mit 10 ml konz. Schwefelsäure abgeraucht, um die aus dem Austauscher eluierte organische Substanz zu zerstören. Wurde dies nicht getan, so wurde bei nachfolgender Kationentrennung der Kationenaustauscher unbrauchbar.

(*d*) Die Beseitigung der Störelemente Eisen, Aluminium usw. mit Cadmiumoxyd und basischem Bleicarbonat wurde nach Ellestad und Horstmann[1] und nach Sweet, Rieman III und Beukenkamp[6] durchgeführt, ehe die Alkalien mit Wofatit KPS 200 getrennt wurden.

Ergebnisse: Wie die Analysenwerte der Tabelle I von zwei Lithiumkonzentraten zeigen, tritt bei reiner Flammenphotometrie derartiger Erzkonzentrate ein erhöhter Li-Wert auf, und zwar bis 8% des Gesamtergebnisses, wenn die Li-Konzentrationen zwischen 2 und 4% Li_2O liegen.

TABELLE I

LITHIUM-GEHALTE DER UNTERSUCHTEN KONZENTRATE

Methode	*Li-Glimmer I (% Li_2O)*	*Li-Glimmer II (% Li_2O)*
a	3.40 ± 0.02	2.67 ± 0.02
c + a	3.22 ± 0.02	2.60 ± 0.02
c + b + a	3.14 ± 0.02	2.44 ± 0.02
d + a	3.36 ± 0.02	—

Die in der Rubrik "Methode" angegebenen Buchstaben sollen das Trenn- und Bestimmungsverfahren, wie bereits beschrieben, angeben. Die gefundenen Gehalte sind die wahrscheinlichsten Werte aus jeweils 50 Analysen. In Testgemischen, die die abzutrennenden Komponenten in gleichen Verhältnissen wie im Glimmer enthielten, wurde das Lithium nach jeder Operation 100%-ig innerhalb der Fehlergrenze wiedergefunden. Die Methode c + b + a ist die Genaueste.

ZUSAMMENFASSUNG

Die flammenphotometrische Bestimmung von Lithium in Zinnwalditkonzentraten wurde nach dem Abtrennen der Störelemente (Fe, Al, Mn, Ca, Mg, K, Na usw.) sowohl mittels Kationen- und Anionenaustauscher als auch mittels CdO oder basischen Bleicarbonates durchgeführt. Die reine Flammenphotometrie gab bis 8% zu hohe Lithiumwerte.

SUMMARY

The flame-photometric determination of lithium in Zinnwaldit-concentrates was carried out after removal of the interfering elements (Fe, Al, Mn, Ca, K, Na, etc.) either by means of cation and anion-exchange resins or by means of CdO or basic lead carbonate. Flame photometry alone resulted in up to 8% too high lithium values.

RÉSUMÉ

Une méthode photométrique de flamme est proposée pour le dosage du lithium dans des silicates. Les ions qui peuvent gêner le dosage sont éliminés soit par échangeurs d'ions, soit au moyen d'oxyde de cadmium ou de carbonate basique de plomb. La photométrie de flamme fournissait des valeurs du lithium jamais jusqu'à 8% trop élevées.

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THE REACTION OF SCHOENBERG'S REAGENT WITH ELEMENTAL SULFUR

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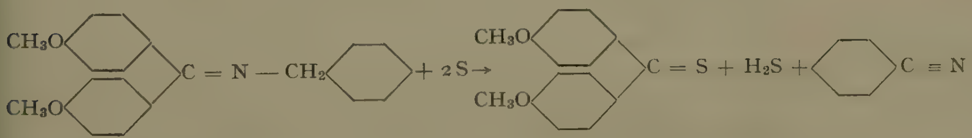
The reaction of elemental sulfur with various diphenyl-substituted compounds has been the object of rather extensive study in recent years, chiefly by Moreau and co-workers[1]. They demonstrated that numerous compounds of this general type will react with sulfur at sufficiently high temperatures, yield H_2S and a corresponding thioketone, and, in certain cases, various other products.

The use of N-4,4′-(dimethoxybenzohydrilidene)benzylamine as a reagent for the detection of elemental sulfur was first proposed by Schoenberg and Urban[2] who observed that this compound could be reacted with elemental sulfur to yield 4,4′-dimethoxythiobenzophenone, H_2S and benzonitrile as recognizable products. The thioketone thus formed was of an intense blue color which was easily recognizable even in small quantities. Although they undertook no quantitative studies of the reaction, they reported the following over-all equation:



The first reported attempt to use the reaction for quantitative determination of sulfur was that of Ory, Warren and Williams[3] who showed that the reaction was quite suitable for colorimetric determinations. The relation between thioketone production and the quantity of sulfur present was not that which would be predicted on the basis of the above equation for the reaction. Instead the thioketone produced corresponded to only about 0.251 of the sulfur present. The absolute quantity of thioketone produced was determined spectrophotometrically using the known optical density of the thioketone[4]. The discrepancy could not be explained on the basis of a deviation from the Beer curve since a plot of optical density *vs.* concentration of thioketone was found to be quite linear. An attempt was made by ORY *et al.*[3] to examine the mechanism of this reaction by a limited number of infrared spectral studies. While not conclusive, the study revealed that the reaction was complex and probably proceeded through one or more intermediates.

From the foregoing, it is seen that the practical application of SCHOENBERG's reagent for quantitative determination of elemental sulfur could be put on a more firm and less semi-empirical basis if an understanding of the mechanism of the reaction could be obtained. The most desirable approach to this problem seems to be that of infrared spectral analysis. Such an analysis of the reagent molecule would itself be of considerable intrinsic value since no extensive study of the benzohydrilidene structure has previously been reported.

The first requirement was to obtain, as completely as possible, an assignment of the infrared absorption spectrum of the reagent, $(CH_3OC_6H_5)_2C{=}NCH_2C_6H_5$. The results of this phase of the study are reported here. Their application to the investigation of the reaction mechanism is being studied further.

TABLE I

Compound	*Group(s) of interest*
Benzylamine	$-CH_2-N$
Benzalazine	$-C{=}N$
Benzylidene aniline	$-C{=}N$
Benzylidene benzylamine	$-C{=}N-CH_2$
Benzylidene methylamine	$-C{=}N-C$
Benzophenone	$-\underset{\|}{C}-$
Benzophenone anil	$-\overset{|}{C}{=}N$
4,4′-diaminobenzophenone	*p,p′*-disubstituted diphenyl
4,4′-dihydroxybenzophenone	*p,p′*-disubstituted diphenyl
4,4′-dimethoxybenzophenone	*p,p′*-dimethoxy diphenyl
4,4′-dimethylbenzophenone	*p,p′*-dimethyl diphenyl
diphenylmethane	$-\overset{|}{\underset{|}{C}}-$
4,4′-dimethoxythiobenzophenone	$CH_3O-\ -\underset{\|}{C}-\ -OCH_3$
p-methyl anisole	$C-\ -OCH_3$
p-methoxy anisole	$-O-CH_3$
Toluene	$-CH_3$

EXPERIMENTAL

Two sampling techniques were used in obtaining the spectrum of SCHOENBERG's reagent:

(*1*) pressed KBr disk technique;

(*2*) solution spectra using CS_2, CCl_4, and benzene as solvents.

Samples of the structurally similar solid compounds were prepared in the same manner. Liquid compounds were examined in thin cells or as films between rock salt plates.

All compounds used were obtained from Eastman Organic Chemicals Company with the exceptions of benzalazine, benzylidene-benzylamine and 4,4′-dimethoxythiobenzophenone which were prepared in these laboratories. The benzalazine was kindly supplied by Dr. HORACE ORY. The benzylidene-benzylamine was prepared by the method of MASON AND WINDER[5]. The 4,4′-dimethoxythiobenzophenone was prepared by the reaction of SCHOENBERG's reagent with elemental sulfur. The thioketone was distilled from the reaction mixture at a temperature of 205° and under pressure of 5 mm Hg.

All solids were purified by recrystallization from ethanol. All liquids were distilled under reduced pressure and the appropriate constant-boiling fraction was collected.

TABLE II

in cm^{-1}	*Assignment*	*in cm^{-1}*	*Assignment*
3030	aromatic CH	1117	CH_3
2941	nonaromatic CH	1050	C—N
2849	$-CH_2-$	1029	C—
1653	$-CH_2-R,\ R \neq H$		
1626 (sh)	C=N	995	mono substituted phenyl
1601	phenyl	943	$-\underset{\vert}{\overset{\vert}{C}}-$
		929	$-\underset{\vert}{\overset{\vert}{C}}-$
1513	*para* substituted phenyl	847	*para* substituted phenyl
1458	phenyl	833	*para* substituted phenyl
1418	CH_3	800	*para* substituted phenyl
1342	OCH_3		
1312	$-\overset{\vert}{C}=$	785	CH_3
1298	C—N	768	$-\overset{\Vert}{C}-$
		749	$-\underset{\vert}{\overset{\vert}{C}}-H$
1250	OCH_3	736	mono substituted phenyl
1181	$-CH_2-$	697	mono substituted phenyl
1173	$-\overset{\vert}{C}=$	685	*para* substituted phenyl
1156	phenyl		

A Perkin-Elmer Model 21 Recording Infrared Spectrometer was used in obtaining all spectral data.

RESULTS AND DISCUSSION

Initial attempts to make definite assignments for all bands based purely on the generalized group frequency assignment given in the widely used chart by COLTHUP and in various standard references[6,7] met with little success. Accordingly, the spectra of a series of compounds having particular structural groupings in common with SCHOENBERG's reagent were examined. The compounds used together with the groups of interest in each are listed in Table I. The presence or absence of bands in the various spectra were then correlated to indicate the probable origin of band. The band frequencies of SCHOENBERG's reagent and their assignments are tabulated in Table II.

A definite suppression of the 847 cm^{-1} band (attributed to *para*-phenyl substitution) was observed in solution spectra of all compounds having this grouping. Spectra of pure liquids having this grouping showed no such suppression nor did there appear to be any in the solid-state spectra. The reason for this is not clearly understood although it presumably results from some type of solvent–solute interaction.

SUMMARY

The infrared absorption spectrum of SCHOENBERG's reagent, $(CH_3OC_6H_5)_2C{=}NCH_2C_6H_5$ has been obtained in the 650–5000 cm^{-1} region. Assignments have been made for all observed bands using group frequency methods.

RÉSUMÉ

Les auteurs ont étudié la réaction du réactif de SCHOENBERG avec le soufre. Le spectre d'absorption infra-rouge de ce réactif a été tracé entre 650 et 5,000 cm^{-1}.

ZUSAMMENFASSUNG

Beschreibung der IR-Spektren des SCHOENBERG'schen Reagenzes zur Bestimmung von Schwefel.

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ON THE USE OF BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AND BIS-ACETALDEHYDE-OXALYLDIHYDRAZONE IN THE ANALYSIS OF COPPER

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INTRODUCTION

In the present publication bis-cyclohexanone-oxalyldihydrazone and bis-acetaldehyde-oxalyldihydrazone will be referred to as reagent 1 and reagent 2, respectively.

NILSSON[1] described the colour formation between copper(II) and the reagents 1 and 2. Other authors applied reagent 1 for the determination of copper in pulp and paper[2], plant materials[3], blood serum[4], steel[5-9], different metals and alloys[9-11] and in gelatine[12]. Some authors[13,14] introduced modifications in their methods of determining copper with reagent 1.

The use of reagent 2 in the analysis of copper is suggested in other papers[9,15], and a procedure has been published for the determination of copper in uranium[16].

The literature surveyed contained no data on the composition and stability of the complexes formed between copper and reagent 1 and 2. The statement by some authors that a considerable excess of reagent 1 was needed to maintain a constant extinction for some time indicated that the complex or the reagent were unstable in solution. An investigation was therefore started with the purpose of obtaining information on the applicability of the two reagents and on the complexes with copper.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000-cm glass cells.

Current–voltage curves were recorded with a Sargent Polarograph Model XXI. The conventional type of dropping mercury electrode and a modified H-cell were used. Oxygen was eliminated before the electrolysis by passing pure nitrogen through the solutions for 10 min. A nitrogen atmosphere was kept over the solutions during electrolyses. An external saturated calomel electrode (SCE) served as reference electrode.

For potentiometric titrations and determinations of pH, a Beckman pH meter model H 2 and a Beckman Zeromatic pH meter were employed.

Reagents

The purity of reagent 1 (Hopkins and Williams Ltd.) was controlled by elementary analysis and infrared absorption spectroscopy. No impurities were detected by these methods.

Reagent 2 was not applied in the solid state, but solutions of the copper(II)–reagent 2 complex were prepared by adding acetaldehyde to solutions of the copper (II)–reagent 1 complex. The higher stability of the former complex resulted in complete replacement of cyclohexanone by acetaldehyde.

The acetaldehyde was of purissimum quality. All other chemicals were of reagent grade quality. Copper-free distilled water was used.

EXPERIMENTAL

Standard solutions

A standard solution of copper(II) was prepared by dissolving 4.4 g of $CuSO_4 \cdot 5H_2O$ in 1000 ml of distilled water and determining the exact concentration by electrolysis. The standard solution was found to contain 1.12 mg of copper per ml corresponding to a molarity of $1.76 \cdot 10^{-2}$.

Reagent 1 is only slightly soluble in water and was therefore dissolved in 50% v/v ethanol. Due to the instability of the reagent only freshly prepared solutions were applied. (Reagent 1 is soluble in aqueous alkaline solutions, but in such solutions the reagent was found to be very unstable.)

Buffer solutions

Buffers consisting of primary and secondary phosphates (which do not form complexes with copper) and of ammonia and ammonium chloride were prepared. The pH of the phosphate buffer was 8.0 and of the two ammonia–ammonium chloride buffers 8.2 and 9.5 (determined by pH meter).

Ionic strength

All solutions prepared were 0.1 *M* with regard to potassium chloride.

Temperature

All experiments were carried out at 20° ± 1°.

Absorption curves

In the pH range 7–10 copper(II) ions react with reagent 1 and 2 forming a blue and a violet complex respectively. In Fig. 1 absorption curves of solutions of the two complexes and of the reagent blank are reproduced, all solutions being measured against distilled water.

It is seen from Fig. 1 that the absorption maximum of the copper(II)–reagent 2 complex varied with the buffer applied. With phosphate buffer (pH 8.0) the maximum was located at 510 mμ, while the use of the ammonia–ammonium chloride buffer (pH 9.5) resulted in a change of maximum to 545 mμ. This change of maximum may be due to the incorporation of ammonium ions in the copper(II)–reagent 2 complex. No similar effect of change of buffer was observed for the copper(II)–reagent 1 complex. (In earlier publications[13] it is stated that ammonium ions affected the colour formation between copper(II) and reagent 1.)

The absorption curves of the copper(II)–reagent 2 complex showed no signs of the presence of copper(II)–reagent I complex.

The different molar extinction coefficients in phosphate buffer pH 8.0 were found to be: $\varepsilon = 1.6 \cdot 10^4$ for the copper(II)–reagent I complex at 600 mμ; and $\varepsilon = 2.3 \cdot 10^4$ for the copper(II)–reagent 2 complex at 510 mμ.

For the copper(II)–reagent 2 complex (ammonia–ammonium chloride buffer pH 9.5) the molar extinction coefficient was found to vary considerably with the excess of reagent used, and therefore no value is given.

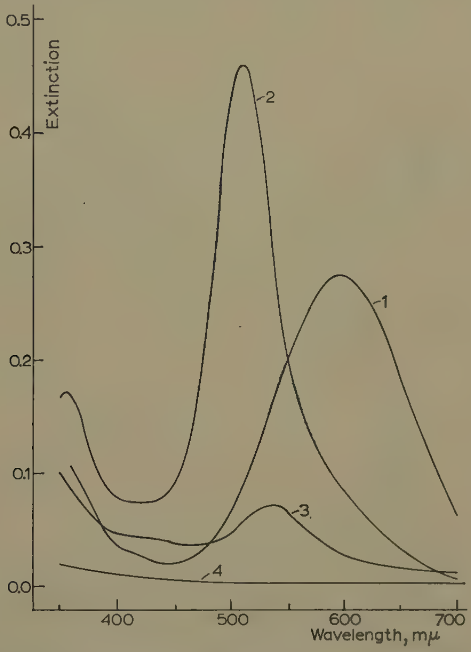


Fig. I. Absorption curves of the copper(II) complexes with reagent I and 2. (I). Absorption curve of the copper(II)–reagent I complex, phosphate buffer pH 8.0; (2). Absorption curve of the copper(II)–reagent 2 complex, phosphate buffer pH 8.0; (3). Absorption curve of the copper(II)–reagent 2 complex, ammonia–ammonium chloride buffer pH 8.2; (4). Absorption curve of a reagent I solution. All solutions were measured against distilled water.

INVESTIGATIONS OF REAGENT I

With the normal four-coordination of copper(II) and presuming the ligand to be bidentate, a ligand–metal ratio of 2:1 was expected for the copper(II)–reagent I complex. Previous authors[4] have reported, however, that in the analysis of copper at least an eightfold excess of reagent I should be added in order to keep the extinction constant for some time. Our own preliminary photometric investigations with the purpose of elucidating the composition of the complex gave inconsistent results indicating the presence of 4–6 ligands. It was further observed that the blue colour of the complex developed slowly, and also that the colour disappeared again after a certain time. The colour faded and disappeared particularly rapidly in the presence of excess of copper.

Investigations by spectrophotometry

A fresh solution of reagent I containing phosphate buffer (pH 8.0) was prepared. From this solution aliquot parts were pipetted into 100-ml volumetric flasks after different times of standing. Copper(II) standard solution was added and the solutions were diluted to volume with distilled water. The concentration of reagent I and copper in the final solutions were $1.408 \cdot 10^{-4}\,M$ and $3.52 \cdot 10^{-5}\,M$, respectively. The extinctions of the solutions were measured at 600 mμ against distilled water after different times of standing at room temperature. From the series of measurements Fig. 2 was plotted.

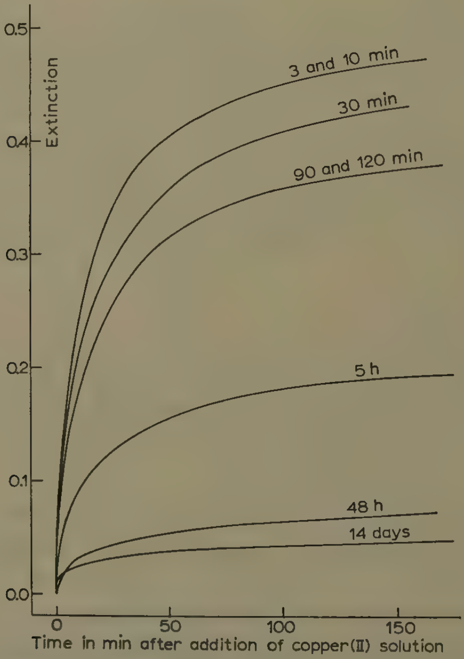


Fig. 2. Extinctions of a series of copper(II)–reagent I solutions measured after the addition of copper(II) solution to reagent I solutions which had been kept in phosphate buffer pH 8.0 for the time specified on the separate curves. All solutions contained $3.52 \cdot 10^{-5}\,M$ of copper and $1.408 \cdot 10^{-4}\,M$ of reagent I. The extinctions were measured at 600 mμ against distilled water.

The experiment showed that the amount of reagent available for colour formation decreased on standing. In the experiment described above the ligand–metal ratio was 4:1. By diminishing the excess of ligand the rate of decomposition on standing increased, the highest rates being observed in the presence of ligand–metal ratios below 2:1.

The experiment also showed that the slow development of the blue colour was not due to complex formation between copper(II) ions and some decomposition product of reagent I. In that case the extinctions measured after the addition of copper(II) ions would be expected to increase with the time of standing of the reagent I solution.

Investigations by polarography

Several polarograms of reagent I in ammonia–ammonium chloride and phosphate buffers were recorded. The polarograms exhibited only one irreversible wave with halfwave potential about —1.6 V *vs.* SCE. (A maximum on the curve was easily depressed by addition of a 0.005% solution of gelatine). It was not possible, however, to obtain a reproducible i_d/c value. The experiments showed that the diffusion current decreased with the time of standing of the reagent I solutions, indicating that the reagent decomposed in solution. No colour was obtained with copper(II) ions after the diffusion current had decreased to a minimum value. Some of the polarographic data are given in Table I.

TABLE I

DIFFUSION CURRENTS AND HALFWAVE POTENTIALS OF A $1.8 \cdot 10^{-3}$ *M* SOLUTION OF REAGENT I IN VARIOUS MEDIA

Buffer	*Time from mixing the solutions*	$E_{1/2}$ *(V vs. SCE)*	i_d *(μA)*
Phosphate, pH 8.0	17 h	—1.59	20.4
	15 d	—1.52	3.1
	37 d	—1.45	2.1
Ammonia–ammonium chloride, pH 8.2	3 d	—1.59	36.4
	15 d	—1.53	8.9
	37 d	—1.50	4.1
Ammonia–ammonium chloride, pH 9.5	1.5 h	—1.57	39.3
	3 d	—1.53	26.2
	7 d	—1.52	19.7
	37 d	—1.50	4.6

The rate of decomposition of the reagent was not reproducible. The decomposition was probably affected also by other factors than the time, *i.e.* pH, ionic strength, temperature, etc. The halfwave potential was found to shift to more positive values when the reagent decomposed. This shift was probably due to some decomposition product(s).

Current–voltage curves of the blue complex and excess of reagent I in ammonia–ammonium chloride and phosphate buffers exhibited two waves. The first wave ($E_{1/2}$ — 0.30 V *vs.* SCE) corresponded to a one-electron reduction of a copper(II) to a copper(I) complex, and the second wave ($E_{1/2}$ — 1.60 V *vs.* SCE) to reduction of the reagent in the complex and of excess of reagent. The plot of log $i/i_d—i$ *vs.* the applied potential for the copper wave showed a straight line with a slope of 0.06 V, indicating a reversible one-electron reduction. The reagent wave showed an irreversible reduction and the diffusion current decreased with the time.

Experiments in ammonia–ammonium chloride buffer containing the blue complex and only a slight excess of reagent I were also performed. Current–voltage curves were recorded at different time intervals after mixing the solutions. The diffusion current of the reagent wave decreased constantly and the wave of tetrammine–copper(II) ions appeared on the polarogram, showing that copper ions were liberated from the complex when the reagent decomposed.

Investigations by pH meter

A $3.27 \cdot 10^{-3}$ *M* solution of reagent I in 50% v/v of ethanol showed a pH of about 3. On titration with sodium hydroxide standard solution (0.1 *N*) the pH increased rapidly to about 8. The titration curve then rose less steeply to an inflection point at about pH 10, corresponding to an addition of 1 equivalent of base. Above pH 10 the curve flattened out.

In another experiment the pH of a $1.8 \cdot 10^{-3}$ *M* solution of reagent I dissolved in 50% v/v of ethanol was adjusted to 8.55 with sodium hydroxide solution. On standing the pH decreased and alkali was added to restore the original pH. On prolonged standing the additions of alkali needed decreased until after about a month the pH was nearly constant and the total amount of base added was nearly 1 equivalent.

In a third experiment a $1.44 \cdot 10^{-3}$ *M* solution of reagent in 50% v/v of ethanol was prepared and hydrochloric acid was added until pH 3.0. On standing, the pH was constant for a month, the only change observed being the appearance of a faint yellow colour.

Reagent I was easily soluble in aqueous sodium hydroxide solutions (pH 10), but the reagent decomposed rapidly and after a relatively short time the solutions did not produce the blue colour with copper(II) ions in the pH range 7–10.

In the pH range 7–10 the addition of copper(II) ions to a solution of reagent I resulted in a drop of pH indicating complex formation with liberation of hydrogen ions.

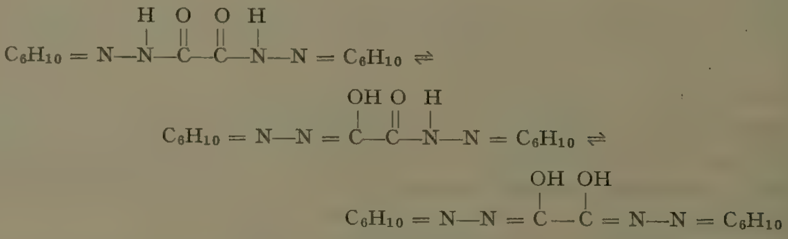
RESULTS AND DISCUSSION

Tautomerism of reagent I

Infrared absorption spectra of reagent I in the solid state showed that the reagent occurred in the ketone form. In an acid solution of reagent I (pH about 3) the presence of the ketone form was indicated qualitatively by precipitation with 2,4-dinitrophenylhydrazine. In strongly alkaline, aqueous solutions (pH > 10) reagent I was believed to be present in the enolic form.

The blue complex between copper(II) and reagent I is stable in the pH range 7–10. In this intermediate pH range reagent I may be present in a partly enolized form.

The following equilibria are suggested for the tautomeric forms of reagent I in solution:



$$C_6H_{10} = N-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-N = C_6H_{10} \rightleftharpoons$$

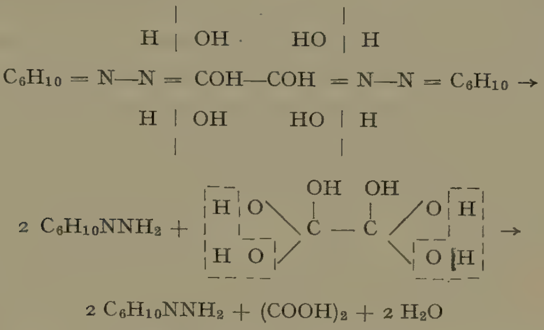
$$C_6H_{10} = N-N = \overset{OH}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-N = C_6H_{10} \rightleftharpoons$$

$$C_6H_{10} = N-N = \overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}} = N-N = C_6H_{10}$$

The slow development of the blue copper(II)–reagent I complex in the pH range 7–10 could be due to a slow enolization of the ketone form.

Decomposition of reagent I

In alkaline aqueous solutions (pH > 10) reagent I decomposed rapidly. Among the decomposition products oxalate ions and reducing agents were detected. The following irreversible decomposition scheme is proposed for reagent I in strongly alkaline solutions:



$$C_6H_{10}=N-N=\overset{H \;|\; OH}{\underset{H \;|\; OH}{COH}}-\overset{HO \;|\; H}{\underset{HO \;|\; H}{COH}}=N-N=C_6H_{10} \rightarrow$$

$$2\ C_6H_{10}NNH_2 + (COOH)_2 + 2\ H_2O$$

According to BALANDIN AND VASKEVICH[17] cyclohexanonehydrazone may react with water:

$$2\ C_6H_{10}NNH_2 + H_2O \rightarrow 2\ C_6H_{11}OH + N_2 + N_2H_4$$

to give cyclohexanol, nitrogen and hydrazine; or, in the presence of catalysts:

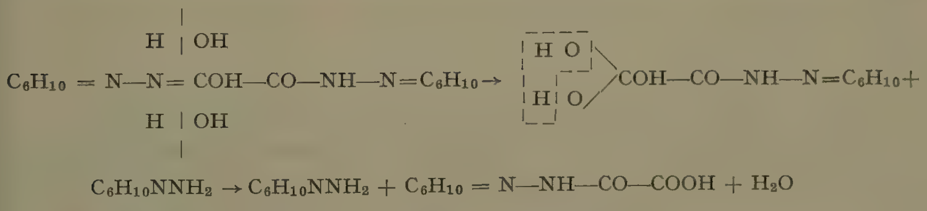
$$C_6H_{10}NNH_2 \rightarrow C_6H_{12} + N_2$$

to form cyclohexane and nitrogen. In the absence of catalysts and in the presence of cyclohexanone, cyclohexanonehydrazone may react as follows:

$$C_6H_{10}O + C_6H_{10}NNH_2 \rightarrow C_6H_{10}NNC_6H_{10} + H_2O$$

Some of these products, *e.g.* hydrazine, are reducing agents.

In the pH range 7–10 acid decomposition products were formed requiring one equivalent of base for neutralization. As in the strongly alkaline range reducing agents were detected, but not oxalate ions. On the basis of these observations the following reaction is suggested for the decomposition of reagent I in the pH range 7–10:



$$C_6H_{10}=N-N=\overset{H \;|\; OH}{\underset{H \;|\; OH}{COH}}-CO-NH-N=C_6H_{10} \rightarrow$$

$$C_6H_{10}NNH_2 \rightarrow C_6H_{10}NNH_2 + C_6H_{10}=N-NH-CO-COOH + H_2O$$

The cyclohexanonehydrazone formed may react further as indicated above producing reducing agents.

In acid solution — pH about 3 — very little decomposition was found to take place. Neither reducing agents nor oxalate ions were detected. A yellow colour appeared, however, on standing, probably originating from a slight decomposition producing cyclohexanone.

The rate of decomposition of reagent I in the pH range 7–10 and above pH 10 was found to increase in the presence of copper(II) ions.

COMPLEX FORMATION OF COPPER WITH REAGENT I

The decomposition of the copper(II)–reagent 1 complex in solution made it difficult to employ the standard spectrophotometric and polarographic methods for elucidating the composition and stability of the complex. With reagent 2, however, the complex formed with copper(II) was stable, and for this complex the ligand–metal ratio of 2:1 was found. Considering the structural similarity between the reagent 1 and the reagent 2 complexes it was deduced that a ligand–metal ratio of 2:1 was highly probable also for the blue complex. The following structure is therefore suggested for the complexes between copper(II) and the reagents 1 and 2.

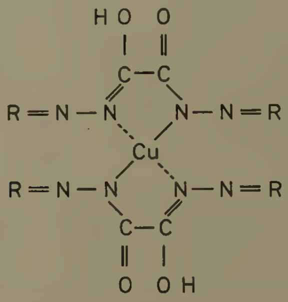


Fig. 3. Suggested structure in solution of the copper(II) complexes with reagent 1 and 2. The group marked R represents either CH_3CH or C_6H_{10}.

The decomposition of reagent 1 in the pH range 7–10 resulted in the formation of reducing agents which in turn may reduce the copper(II) ions. By polarography the presence of a colourless copper(I)–reagent 1 complex was indicated, but due to the instability of the system detailed investigations could not be carried out. As seen below a copper(I)–reagent 2 complex with 2 ligands was found polarographically, and this number of ligands is also probable for the similar copper(I)–reagent 1 complex.

Finally, complexes between copper and reagent 1 may exist in the acid and strongly alkaline range.

INVESTIGATIONS OF REAGENT 2 AND THE COPPER–REAGENT 2 COMPLEXES

Solutions of the complex between copper(II) and reagent 2 were prepared by mixing known volumes of solutions of copper(II) ions, reagent 1, phosphate buffer (pH 8.0) and excess of acetaldehyde. The colour of the blue complex appeared initially, but in the course of seconds the solution turned violet. The replacement of cyclohexanol by acetaldehyde was found to be complete as seen by the absorption curves of the complexes. The violet complex was found to be stable in the pH range 6–10.

The extinctions of solutions of the copper(II)–reagent 2 complex increased rapidly after preparation and reached a maximum after about 48 h at room temperature. The extinctions were then constant for months. In the presence of ammonium ions the extinctions decreased slowly on standing.

The stability of the violet complex in solution made possible a determination of the composition by the method of continuous variation, and a distinct maximum was obtained for the ligand–metal ratio 2:1. The molar ratio method confirmed this composition.

Qualitative experiments indicated that the violet complex had a stability constant intermediate between the copper(II)–ethylenediaminetetraacetate complex (log $K = 16.2$ at pH 8.0) and the copper(II)–cyanide complex (log $K = 25$). Attempts to calculate the stability constant from spectrophotometric data gave log K-values which were apparently too low (log K about 10).

Current–voltage curves of the violet copper(II) complex exhibited three waves. The first wave corresponded to reduction of copper in the complex. The second and third wave were due to reduction of excess of acetaldehyde and of reagent 2, respectively. The irreversible reagent wave was partly overlapped by the acetaldehyde wave in solutions containing a large excess of the latter reagent.

In ammonia–ammonium chloride buffer the halfwave potential of the copper wave in the complex was —0.30 V *vs.* SCE. Tetrammine-copper(II) ions in the same medium are reduced at a more positive potential. Consequently, it was possible to determine excess of copper in the presence of copper(II) complex. Polarograms of several solutions containing copper and different amounts of reagent 2 were recorded, and the diffusion current of tetrammine-copper(II) ions was plotted against the ligand–metal ratio of the solutions. The diffusion current of copper(II) decreased linearly with increasing amounts of reagent 2 and became equal to the residual current at the ligand–metal ratio 2:1 in accordance with the result obtained by spectrophotometry.

Several polarograms of the complex in ammonia–ammonium chloride and phosphate buffers and with a varying excess of reagent 2 were recorded. In all solutions the plot of log $i/i_d—i$ *vs.* the potential of the copper wave showed a straight line with the slope 0.06 indicating a reversible one-electron reduction to a copper(I) complex. The halfwave potential was constant independent of the supporting electrolyte and of excess of reagent 2 showing a ligand–metal ratio of 2:1 also for the copper(I) complex. This complex is probably colourless, as it was not detected with the spectrophotometer.

The possible structure of the copper(II)–reagent 2 complex is shown in Fig. 3 (*vide supra*).

The violet complex between copper(II) and reagent 2 has been found to be much more stable in the solutions examined than the corresponding blue complex, and it has a higher molar extinction coefficient, is easily prepared and is therefore to be recommended for spectrophotometric determination of copper.

ACKNOWLEDGEMENT

The authors are indebted to PROF. HAAKON HARALDSEN for his interest in this investigation and for the facilities placed at their disposal.

SUMMARY

The reagents bis-cyclohexanone-oxalyldihydrazone (reagent 1) and bis-acetaldehyde-oxalyldihydrazone (reagent 2) and their complexes with copper were examined by spectrophotometry and polarography. The investigations indicated that in solution reagent 1 existed in three tautomeric forms depending of the pH of the solvent. The decomposition of these forms was studied and decomposition schemes are suggested. In the pH range employed for spectrophotometric determination of copper (7–10), solutions of reagent 1 and the copper(II)–reagent 1 complex were found to be very unstable owing to the decomposition of the ligand. Solutions of reagent 2 and its complexes with copper were found to be much more stable. The investigations further indicated that both reagents form copper(II) complexes with ligand–metal ratios 2:1. In addition a colourless copper(I)–reagent 2 complex with two ligands was found polarographically. The existence of a similar complex between copper(I) and reagent 1 is probable.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique et polarographique des complexes du cuivre, obtenus avec les deux réactifs suivants: bis-cyclohexanone-oxalyldihydrazone (réactif 1) et bis-acétaldéhyde-oxalyldihydrazone (réactif 2). Le réactif 1 peut exister sous trois formes tautomères, suivant le pH; les solutions du réactif 2 et de ses complexes avec le cuivre sont plus stables que celles du réactif 1.

ZUSAMMENFASSUNG

Untersuchung über die Verwendung von Bis-cyclohexanon-oxalyl-dihydrazon (Reagenz 1) und Bis-acetaldehyd-oxalyl-dihydrazon (Reagenz 2) zur spectrophotometrischen und polarographischen Bestimmung von Kupfer. Reagenz 1 existiert in 3 tautomeren Formen in Abhängigkeit von pH und Lösungsmittel. Es fölgen Angaben über die Zusammensetzung der Komplexe und deren Stabilität.

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Short Communications

Determinations of stability constants

The following method allows the determination of stability constants for complexes containing no more than two ligands, without the need to resort to graphical procedures. In the particular case chosen, the concentration of the ion under investigation was determined potentiometrically.

Solutions are said to be "corresponding" when they differ in C_M (total concentration of metal) and C_L (total concentration of ligand) but have the same average ligand number, $\bar{n}$. It has been shown[1], that if for two solutions the ratio metal : ligand is changed until the potential difference (E_M) due to the formation of complex is the same for both, the solutions are "corresponding".

$$\begin{aligned} E_M &= E_0 - E \\ &= \left(E_k + \frac{RT}{nF}\ln C_M\right) - \left(E_k + \frac{RT}{nF}\ln [\mathrm{M}]\right) \\ &= \frac{RT}{nF}\ln\frac{C_M}{[\mathrm{M}]} \end{aligned}$$

E_0 = e.m.f. of cell when no ligand has been added
E = e.m.f. of cell after addition of ligand
E_k includes the potential of the reference electrode, liquid junction potential, and activity coefficients.

$C_M/[\mathrm{M}]$ can thus be determined for when the solutions are "corresponding". For corresponding solutions

$$\bar{n} = \frac{C_L' - C_L}{C_M' - C_M}$$

and thus $\bar{n}$ can be determined. For a complex containing only two ligands

$$\bar{n} = 2 - \frac{[\mathrm{ML}]}{C_M} - \frac{2[\mathrm{M}]}{C_M}$$

$[\mathrm{M}]/C_M$ and $\bar{n}$ are both known so that [ML] can be calculated. All the information required to calculate the stability constants β_1 and β_2 is now available.

The above method was applied to the silver–pyridine system, the silver ion concentration being determined by means of a silver–silver bromide electrode, the reference electrode being a calomel electrode. The following values were obtained at 25°, the ionic strength of the solution being maintained at 0.1 by addition of the requisite amount of potassium nitrate:

$$\log \beta_1 = 1.90$$

$$\log \beta_2 = 4.25$$

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[1] Sten Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, (1958) 264.

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Elimination of aluminium interference in colorimetric determination of fluoride in water

Aluminium and fluoride when present together in natural water form a complex of great stability which interferes in the colorimetric determination of fluoride by the zirconium-alizarin method. For this determination MEGREGIAN[1] used correction curves, implying the previous determination of aluminium. To avoid that determination and eliminate the aluminium interference we have developed a separation by solvent extraction.

Precipitation of aluminium 8-hydroxyquinolate in presence of ammonium ions has been reported to separate aluminium from phosphorus, arsenic, fluorine and boron[2]. According to GENTRY AND SHERRINGTON[3] a 1% solution of 8-hydroxyquinoline in chloroform gives complete extraction of aluminium from an aqueous layer. The chloroform layer can be separated and its absorbance measured for aluminium. Studying the pH effect the same authors found that extraction is complete in two pH ranges: from 4.5–6.5 and from 8–11.5.

It thus seemed possible to use 8-hydroxyquinoline in chloroform to separate aluminium from fluoride, both in trace concentrations. Natural water is first buffered at pH 10 and then extracted, the aqueous layer being analysed for fluoride. The fluoride contents of many natural water samples showed good agreement with previous results and no effect of aluminium interference.

Procedure

Place in a 250-ml separatory funnel 25 ml of water with 1.2038 g of powdered ammonium chloride and 22.5 ml of 1 *M* ammonium hydroxide to buffer the solution at pH 10. Dilute the volume to 50 ml with distilled water. Add 10 ml of a 1% solution of 8-hydroxyquinoline in chloroform and shake the funnel steadily for 6 min. Allow the layers to settle, and run off the organic layer. Then remove the aqueous layer to a 100-ml stoppered flask, and adjust its pH to 5–7 with 1 : 1 hydrochloric acid. Fluoride is then colorimetrically determined by the zirconium-alizarin method.

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[1] S. MEGREGIAN AND F. J. MAIER, *J. Am. Water Works Assoc.*, 44 (1952) 239.

[2] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMAN, *Applied Inorganic Analysis*, John Wiley and Sons, New York, 1953.

[3] C. H. R. GENTRY AND L. G. SHERRINGTON, *Analyst*, 71 (1949) 432.

Received February 24th, 1961

Book Review

The Analysis of Titanium and its Alloys, 3rd ed., Imperial Chemical Industries Ltd., London, 1959, 119 pp., price 21 s.

The appearance of a third edition of this book in less than three years indicates the importance of the subject under consideration and also of the usefulness and quality of this work.

As in the previous editions, one or more reliable analytical procedures are described in detail for each of more than twenty-five elements which can be present in titanium alloys. Also included are sampling procedures for the various forms of titanium metal and a semi-quantitative spectrographic identification method. An additional chapter is devoted to the identification of titanium alloys by means of simple, non-destructive spot tests on the metal surface.

Some of the earlier procedures have been modified or replaced by quicker or more convenient methods. An entirely new amperometric method for the determination of chlorine replaces the turbidimetric method. A procedure for determining boron, a more sensitive method for the analysis of nitrogen, an additional procedure for determining carbon, a differential absorptiometric procedure for the determination of large amounts of molybdenum and some others appear for the first time.

This third edition is strongly recommended to all chemists with analytical problems involving titanium and its alloys.

F. VERBEEK (Ghent)

Anal. Chim. Acta, 24 (1961) 591

Announcements

THE GORDON RESEARCH CONFERENCES

12 June–1 September 1961

The Gordon Research Conferences for 1961 will be held from 12 June to 1 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire; Kimball Union Academy, Meriden, New Hampshire; and Tilton School, Tilton, New Hampshire.

Purpose. The conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and discussion groups.

It is hoped that each conference will extend the frontiers of science by fostering a free and informal exchange of ideas among persons actively interested in the subjects under discussion. The purpose of the program is to bring experts up to date on the latest developments, to analyze the significance of these developments and to provoke suggestions concerning the underlying theories and profitable methods of approach for making progress. The review of known information is not desired.

Registration and reservations. Attendance at the Conferences is by application. Individuals interested are requested to send their applications to the Director at least two months prior to the date of the Conference. *All applications must be submitted in duplicate on the standard application form which may be obtained by writing to the office of the Director.* This procedure is important because certain specific information is required in order that a fair and equitable decision on the application may be made. Attendance at each Conference is limited to approximately 100 conferees.

The Board of Trustees of the Conferences has established a fixed fee of $100 for resident conferees at each Conference. The fixed fee will cover registration, room (except room with private bath or single room), meals and gratuities. Conferees living at the Conference location who will pay all or part of the fixed fee as a personal expense may request a reduction of $25 in the fixed fee. Application for this special fee ($75) must be made when the registration card is returned to the Director.

Limited accommodation is available for wives and families.

Attendance. Requests for attendance at the conferences, or for additional information, should be addressed to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From 12 June to September 1961 mail for the office of the Director should be addressed to Colby Junior College, New London, New Hampshire.

The program of the *Analytical Chemistry Conference* which will be held on 14–18 August 1961 at New Hampton School, New Hampton, N.H., with SIDNEY SIGGIA as Chairman, and DONALD D. DEFORD as Vice-Chairman, is as follows:

14 Aug.
    C. B. MURPHY, Differential Thermal Analysis.
    D. J. FRAADE, Continuous Analysis.

15 Aug.
    I. FANKUCHEN, The Application of X-Rays to Structure Determination of Organic Materials.
    L. S. BIRKS, The Electron Probe.

16 Aug.
    H. FISCHBACH, J. W. COOK, L. L. RAMSEY, Analysis and Food and Drug Regulations.
    W. W. BATES, Analysis and Composition of Tobacco Smoke.

17 Aug.
    J. E. LOVELOCK, Electron Affinity Spectroscopy.
    Open Session.

18 Aug.
    G. A. HARLOW, New Developments in the Determination of Acids and Bases.

Other conferences will be held on Petroleum, Catalysis, Polymers, Textiles, Elastomers, Corrosion, Medicinal Chemistry, Separation and Purification, Instrumentation, Food and Nutrition, Cancer, Chemistry of Coal, Chemistry and Physics of Liquids, Proteins, Scientific Information Problems, Magnetic Resonance, Radiation Chemistry, Organic Reactions, Steroids and other Natural Products, Statistics in Chemistry and Chemical Engineering, Inorganic Chemistry, Adhesion, Lipid Metabolism, Cell Structure and Metabolism, Physical Metallurgy, Vitamins and Metabolism, Chemistry etc. of Bones and Teeth, Organic Coatings, Chemistry at Interfaces, Solid State Studies in Ceramics, Toxicology and Safety, Chemistry and Physics of Solids, Photonuclear Reactions, High Temperature Chemistry, Ion Exchange, Chemistry and Metallurgy of Semiconductors, Microbiological Deterioration, Biochemistry and Agriculture, Electrodeposition, Glass.

JOINT CONFERENCES
NUCLEAR REACTOR CHEMISTRY
ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

The Second Conference on Nuclear Reactor Chemistry and the Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tenn. (U.S.A.), on October 10, 11 and 12, 1961, under the sponsorship of Oak Ridge National Laboratory which is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Second Conference on Nuclear Reactor Chemistry. The chemical behavior of reactor materials will be emphasized at this conference. Subjects for discussion include: chemical behavior of moderator and coolant materials and the effects of nuclear radiation on their properties; deportment of fission products in reactor fuels; development of reactor fuel and blanket materials; the application of statistical methods and computer calculations in planning and evaluation of experiments. Papers on these and other topics of interest to reactor chemists will be welcomed.

Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology. This conference will be devoted to improved methods and instruments for the analysis of many nuclear materials and products. Papers are especially solicited on the following or related subjects: measurements of burn-up of uranium or plutonium fuels; isotopic analysis; determination of gases in reactor materials; methods and instruments for on-line analyses; remote analysis of radioactive materials; non-destructive testing of nuclear fuel elements and other reactor materials; analysis of (*a*) Be, BeO, cermets containing BeO, (*b*) Zr and Nb alloys, (*c*) heavy water, (*d*) plutonium and plutonium-base fuels.

In addition to papers setting forth specific achievements, review papers critically evaluating the *state of the art* with respect to any of the foregoing subjects are solicited.

Authors are requested to submit an abstract of 200 to 400 words of their paper, not later than July 15, 1961, and, at the same time, to indicate the time required for the presentation, not to exceed 20 minutes.

Proceedings of these conferences are to be published. Manuscripts of papers for publication should be submitted prior to or at the time of the conferences.

Abstracts of papers and inquiries regarding these conferences should be directed to the Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. (U.S.A.), Attention:

W. R. GRIMES for Nuclear Reactor Chemistry

and

C. D. SUSANO for Analytical Chemistry

Inquiries concerning lodging or requests for reservations should be directed to: Reservation Services, Chamber of Commerce, Gatlinburg, Tenn. (U.S.A.).

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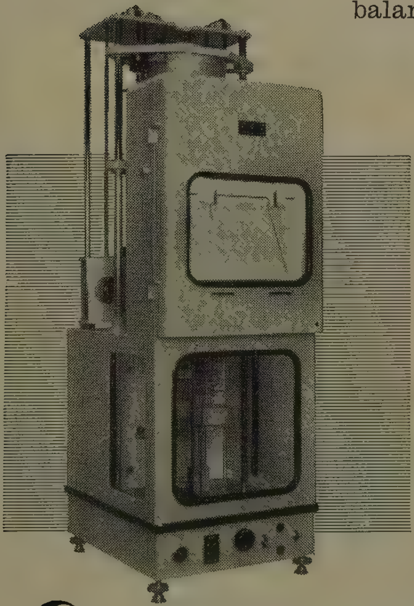

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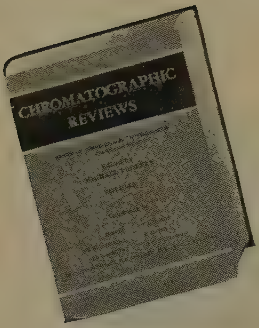

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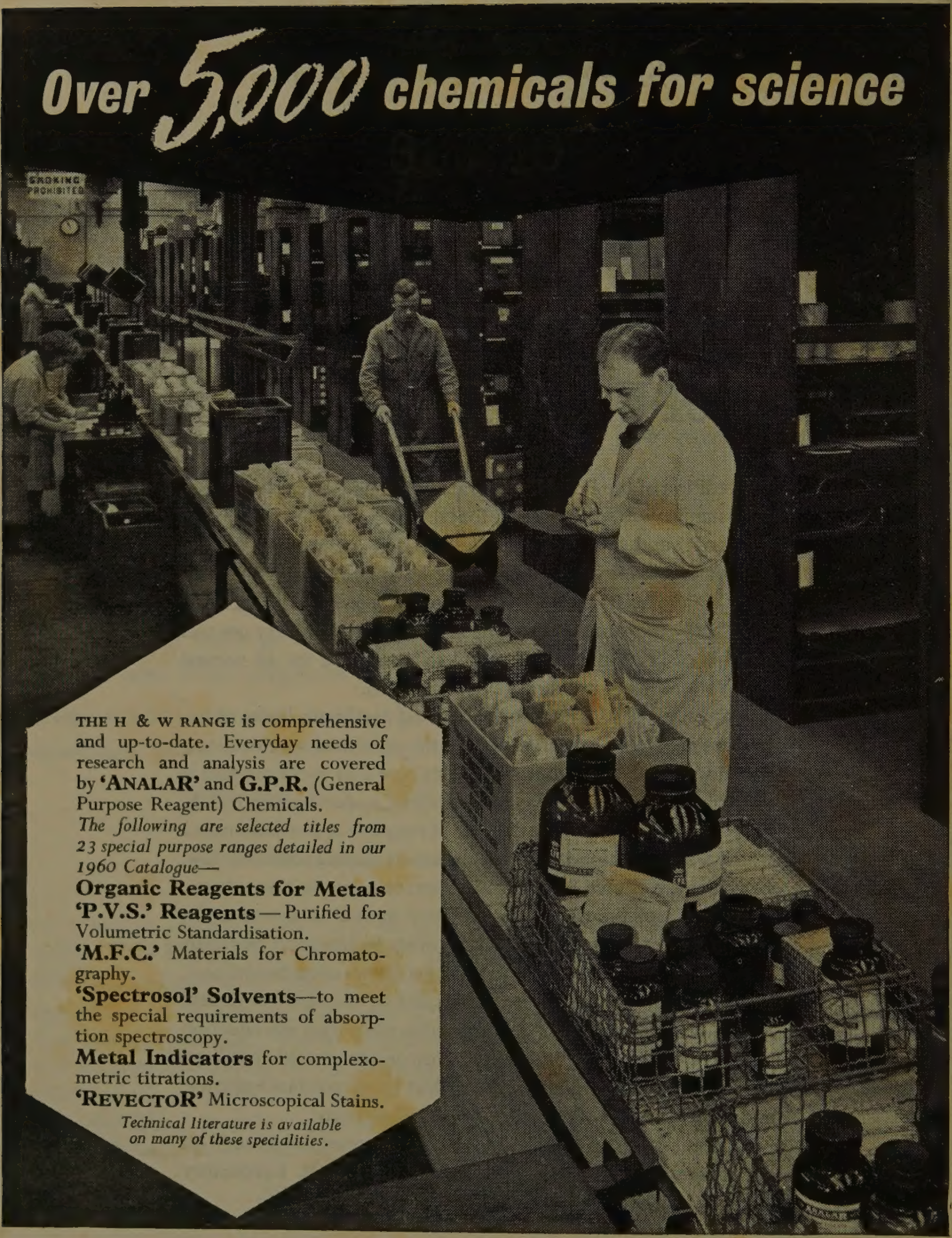
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